

Electronic Supplementary Information

Arylation of Benzyl Amines with Aromatic Nitriles

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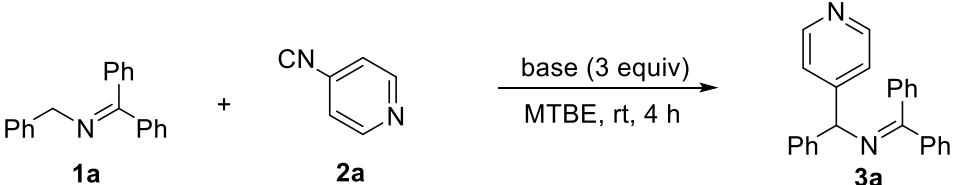
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1. General information

Unless stated otherwise, all reactions were carried out under an argon atmosphere. All chemicals obtained from the commercial suppliers, MTBE, DME were used without further purification, the other solvents were purified and dried by standard methods prior to use. Reactions were monitored by thin layer chromatography (TLC). Column chromatography purifications were carried out using silica gel GF254. ^1H NMR (300 MHz), ^{13}C NMR (75 MHz or 101MHz), and ^{19}F NMR (282 MHz or 376MHz) spectra were recorded on a Varian instrument spectrometer in CDCl_3 or DMSO, respectively. Data for ^1H NMR were recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad, q = quartet, coupling constant(s) in Hz integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ , ppm). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources.

2. Optimization of reaction conditions

a) Table S1. Screening of basic additives^a



Entry	Base	yield (%)	Entry	Base	yield (%)
1	LiO^tBu	0	8	TMEDA	0
2	NaO^tBu	0	9	DMAP	0
3	KO^tBu	0	10	DBU	0
4	K_2CO_3	0	11	NaHDMS	40
5	Na_2CO_3	0	12	LiHDMS	28
6	NaOAc	0	13	KHDMS	18
7	Et_3N	0			

^a Reaction conditions: Unless otherwise noted, reactions were conducted on a 0.2 mmol scale using 2 equiv of **1a**, 3 equiv of base, and 1 mL solvent. Yields were determined by ^1H NMR spectroscopy of the reaction mixture using mesitylene as internal standard.

b) Table S2. Screening of solvents^a

Reaction scheme: Ketimine **1a** (Ph-CH₂-N=C(Ph)₂) reacts with 4-cyanopyridine **2a** (4-CN-pyridine) in the presence of NaHMDS (3 equiv) at room temperature (rt) for 4 hours to yield the arylated ketimine **3a** (4-(2-phenyl-1-phenylvinyl)pyridine).

Entry	Solvent	yield (%)	Entry	Solvent	yield (%)
1	MTBE	40	7	CHCl ₃	0
2	DMF	trace	8	acetone	9
3	DME	72	9	EtOH	trace
4	DMSO	7	10	PhCl	0
5	DCM	0	11	MeCN	0
6	DCE	0	12	EtOAc	0

^a Reaction conditions: Unless otherwise noted, reactions were conducted on a 0.2 mmol scale using, 2 equiv of **1a** and 1 mL solvent. NaHMDS 2M in THF was used. Yields were determined by ¹H NMR spectroscopy using mesitylene as internal standard.

3. General procedure for the synthesis of ketimines and aromatic nitriles

Ketimines¹ and aromatic nitriles^{2,3} were prepared according to the literature procedures.

4. General procedure for the arylation reactions

To an oven-dried 10 mL glass vial with a magnetic stirring bar was added ketimines **1** (0.8 mmol) and 4-cyanopyridine **2** (0.4 mmol), sealed with a rubber septum. Then, the air was withdrawn and backfilled with argon (three times). NaHMDS (0.8 mmol, 2.0 mol/L in THF) and 2 mL of anhydrous DME were added to the reaction by syringes, respectively. The reaction was stirred at room temperature for 12 h, and then, quenched with two drops of H₂O, diluted with 10 mL of ethyl acetate, and filtered over a pad of MgSO₄ and silica. The pad was rinsed with an additional 20 mL of ethyl acetate (2 x 10 mL). The combined solutions were concentrated *in vacuo* and purified by a silica gel column chromatography (eluted with *n*-hexane/ethyl acetate 20:1-3:1) to afford the product.

5. Gram scale sequential one-pot ketimine synthesis and arylation procedure

An oven-dried 100 mL round bottom flask equipped with a stir bar was sealed with a rubber septum. The air was withdrawn and backfilled with argon (three times). DCM (10 mL) was added via syringe through the rubber septum. 2-furfurylamine (0.97 g, 10.0 mmol) and benzophenone imine (1.81 g, 10.0 mmol) were added under nitrogen via syringe through the rubber septum. The reaction was stirred at 23 °C for 18 h. The solvent was completely

removed *in vacuo* and the flask was filled with argon. A solution of 4-cyanopyridine **2a** (0.52 g, 5.0 mmol) in 25 mL anhydrous DME was added to the flask tube via syringe through the rubber septum. Next, NaHMDS (10 mmol, 2.0 mol/L in THF) was added by syringe through the rubber septum. The reaction mixture was stirred for 12 h at room temperature, then, quenched with 10 mL of H₂O. The layers were separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were concentrated *in vacuo*. The crude material was purified by a silica gel column chromatography (eluted with n-hexane/ethyl acetate 20:1-3:1) to give the product (1.03 g, 61% yield) as a thick colorless oil.

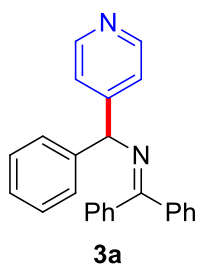
6. Imine product hydrolysis

An oven-dried 10ml vial equipped with a stir bar was charged with **3s** (40.7 mg 0.1 mmol). THF (1 mL) was added to the reaction vial via syringe and the reaction was cooled to 0 °C. HCl (1 mL, 1 N) was added to the reaction vial via syringe. The solution was warmed to room temperature and monitored by TLC until **3s** was totally consumed (reaction completed in 3 h). The reaction mixture was basified with 1 N NaOH until the pH reached 14. The the mixture was transferred to a 30 ml seperatory funnel and extracted with dichloromethane (3 x 2 mL). The combined organic layers were concentrated *in vacuo* and purified on a silica gel column chromatography (eluted with hexanes:ethyl acetate = 2:1) to give the amine product **4** as a yellow oil (23.3 mg, 96% yield).

7. References

- 1) M. Hatano, Y. Hattori, Y. Furuya and K. Ishihara, *Org. Lett.*, 2009, **11**, 2321.
- 2) L. B. Seiple, S. Su, R. A. Rodriguez, R. Gianatassio, Y. Fujiwara, A. L. Sobel and P. S. Baran, *J. Am. Chem. Soc.*, 2015, **137**, 13902.
- 3) J. D. Galloway, D. N. Mai, and R. D. Baxter, *Org. Lett.*, 2017, **19**, 1084.

8. Characterization of products

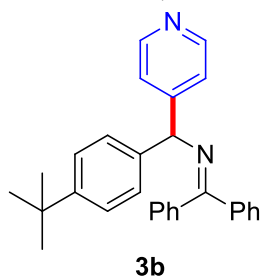


N-(diphenylmethylene)-1-phenyl-1-(pyridin-4-yl)methanamine (**3a**), 122.7 mg, yield: 88%. White solid, mp 117-119 °C.

¹H NMR (300 MHz, CDCl₃) δ 8.50 (d, *J* = 6.0 Hz, 2H), 7.75 (d, *J* = 6.7 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.43 – 7.35 (m, 3H), 7.35 – 7.27 (m, 7H), 7.09 – 7.00 (m, 2H), 5.50 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 168.27, 153.46, 149.79, 143.24, 139.36, 136.29, 130.41, 128.75, 128.72, 128.58, 128.54, 128.08, 127.61, 127.52, 127.26, 122.48, 68.92.

HRMS (ESI): C₂₅H₂₀N₂+H⁺ Calcd: 349.1699, Found: 349.1703.

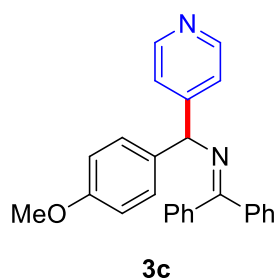


1-(4-(tert-butyl)phenyl)-*N*-(diphenylmethylene)-1-(pyridin-4-yl)methanamine (**3b**), 121.4mg, yield: 75%. Thick colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 8.42 (d, *J* = 5.7 Hz, 2H), 7.67 (d, *J* = 6.7 Hz, 2H), 7.42 – 7.32 (m, 4H), 7.32 – 7.22 (m, 5H), 7.20 – 7.12 (m, 3H), 7.03 – 6.91 (m, 2H), 5.41 (s, 1H), 1.21 (s, 9H).

¹³C NMR (75 MHz, CDCl₃) δ 168.00, 153.81, 150.09, 149.53, 140.09, 139.40, 136.30, 130.35, 128.69, 128.52, 128.06, 127.58, 127.19, 125.48, 122.57, 68.68, 34.44, 31.35.

HRMS (ESI): C₂₉H₂₈N₂+H⁺ Calcd: 405.2325, Found: 405.2326.

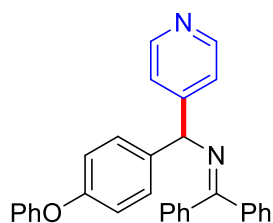


N-(diphenylmethylene)-1-(4-methoxyphenyl)-1-(pyridin-4-yl)methanamine (**3c**), 116.6mg, yield: 77%. White solid, mp 91-92°C.

¹H NMR (300 MHz, CDCl₃) δ 8.49 (d, *J* = 6.0 Hz, 2H), 7.74 (d, *J* = 6.7 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.42 – 7.30 (m, 4H), 7.25 – 7.14 (m, 3H), 7.11 – 6.98 (m, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.46 (s, 1H), 3.78 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.99, 158.79, 153.82, 149.81, 139.47, 136.41, 135.55, 130.40, 128.77, 128.73, 128.57, 128.48, 128.12, 127.59, 122.46, 114.00, 68.33, 55.26.

HRMS (ESI): C₂₆H₂₂N₂O+H⁺ Calcd: 379.1805, Found: 379.1803.



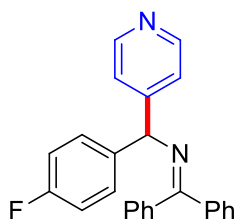
3d

N-(diphenylmethylene)-1-(4-phenoxyphenyl)-1-(pyridin-4-yl)methanamine (**3d**), 98.7mg, yield: 56%. Thick colorless oil.

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.51 (d, $J = 6.0$ Hz, 2H), 7.75 (d, $J = 6.7$ Hz, 2H), 7.51 – 7.36 (m, 6H), 7.36 – 7.27 (m, 5H), 7.15 – 6.85 (m, 8H), 5.48 (s, 1H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 168.27, 156.97, 156.47, 153.54, 152.71, 149.74, 139.33, 138.03, 136.29, 130.47, 129.71, 128.94, 128.76, 128.59, 128.12, 127.51, 123.32, 122.43, 118.98, 118.78, 68.32.

HRMS (ESI): $\text{C}_{31}\text{H}_{25}\text{N}_2\text{O}+\text{H}^+$ Calcd: 441.1961, Found: 441.1963.



3e

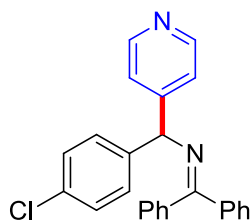
N-(diphenylmethylene)-1-(4-fluorophenyl)-1-(pyridin-4-yl)methanamine (**3e**), 99.7mg, yield: 68%. Thick colorless oil.

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.51 (d, $J = 4.4$ Hz, 2H), 7.75 (d, $J = 7.1$ Hz, 2H), 7.48 – 7.42 (m, 3H), 7.43–7.51 (m, 3H), 7.34 – 7.42 (m, 4H), 7.08 – 6.93 (m, 4H), 5.48 (s, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.49, 161.95 (d, $J_{\text{C-F}} = 247.5$ Hz) 153.26, 149.86, 139.23, 139.03 (d, $J_{\text{C-F}} = 4.0$ Hz) 136.22, 130.53, 129.19, 129.11, 128.81, 128.75, 128.61, 128.13, 127.44, 122.37, 115.44 (d, $J_{\text{C-F}} = 21.2$ Hz) 68.13.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -115.12.

HRMS (ESI): $\text{C}_{25}\text{H}_{19}\text{FN}_2+\text{H}^+$ Calcd: 367.1605, Found: 367.1611.



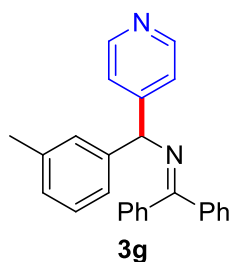
3f

1-(4-chlorophenyl)-*N*-(diphenylmethylene)-1-(pyridin-4-yl)methanamine (**3f**), 108.7mg, yield: 71%. Thick colorless oil.

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.51 (d, $J = 5.8$ Hz, 2H), 7.74 (d, $J = 7.0$ Hz, 2H), 7.48 – 7.33 (m, 6H), 7.29 – 7.22 (m, 6H), 7.07 – 6.96 (m, 2H), 5.47 (s, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.73, 152.97, 149.91, 141.76, 139.18, 136.17, 133.09, 130.58, 128.94, 128.85, 128.76, 128.63, 128.15, 127.43, 122.38, 68.21.

HRMS (ESI): $\text{C}_{25}\text{H}_{19}\text{ClN}_2+\text{H}^+$ Calcd: 383.1310, Found: 383.1311.

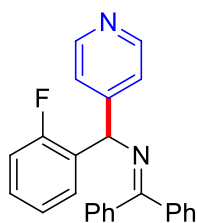


N-(diphenylmethylene)-1-(pyridin-4-yl)-1-(*m*-tolyl)methanamine (**3g**), 114.5mg, yield: 79%. Thick colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 8.41 (d, *J* = 5.9 Hz, 2H), 7.67 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.39 – 7.23 (m, 6H), 7.22 – 7.15 (m, 2H), 7.13 – 7.06 (m, 1H), 7.03 – 6.92 (m, 5H), 5.39 (s, 1H), 2.22 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 168.17, 153.65, 149.73, 149.60, 143.11, 139.37, 138.21, 136.28, 130.36, 128.69, 128.49, 128.41, 128.24, 128.04, 127.53, 124.64, 122.48, 68.95, 21.52.

HRMS (ESI): C₂₆H₂₂N₂+H⁺ Calcd: 363.1856, Found: 363.1860.



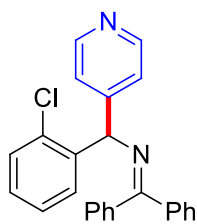
N-(diphenylmethylene)-1-(2-fluorophenyl)-1-(pyridin-4-yl)methanamine (**3h**), 98.2mg, yield: 67%. Thick colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 8.50 (d, *J* = 5.2 Hz, 2H), 7.72 (dd, *J* = 17.8, 7.1 Hz, 3H), 7.46 – 7.28 (m, 8H), 7.23 – 7.10 (m, 2H), 6.98 (dd, *J* = 18.1, 8.4 Hz, 3H), 5.86 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.33, 159.56 (d, *J*_{C-F} = 247.5 Hz) 152.61, 149.85, 139.33, 136.16, 130.55, 129.33 (d, *J*_{C-F} = 4.0 Hz) 128.81, 128.69, 128.74 (d, *J*_{C-F} = 9.09 Hz), 128.13, 127.37, 124.50 (d, *J*_{C-F} = 4.0 Hz) 115.34 (d, *J*_{C-F} = 22.2 Hz) 61.48.

¹⁹F NMR (376 MHz, CDCl₃) δ -118.18.

HRMS (ESI): C₂₅H₁₉FN₂+H⁺ Calcd: 367.1605, Found: 367.1613.

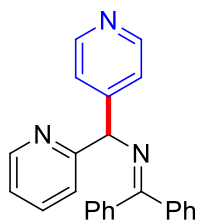


1-(2-chlorophenyl)-*N*-(diphenylmethylene)-1-(pyridin-4-yl)methanamine (**3i**), 107.2mg, yield: 70%. Thick colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 8.49 (d, *J* = 5.4 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.33 (m, 6H), 7.33 – 7.26 (m, 4H), 7.21 – 7.14 (m, 1H), 7.06 – 6.96 (m, 2H), 6.05 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.35, 152.40, 149.79, 140.94, 139.30, 136.30, 132.46, 130.53, 130.15, 129.41, 128.82, 128.79, 128.60, 128.36, 128.11, 127.42, 127.31, 122.49, 64.48.

HRMS (ESI): C₂₅H₁₉ClN₂+H⁺ Calcd: 383.1310, Found: 383.1317.



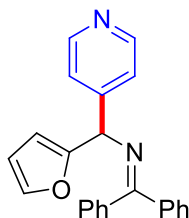
3j

N-(diphenylmethylene)-1-(pyridin-2-yl)-1-(pyridin-4-yl)methanamine (**3j**), 76.9mg, yield: 55%. Thick colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 8.46 (d, $J = 4.8$ Hz, 1H), 7.86 – 7.73 (m, 3H), 7.67 (td, $J = 7.7$, 1.7 Hz, 1H), 7.43 – 7.35 (m, 7H), 7.35 – 7.27 (m, 2H), 7.23 – 7.15 (m, 1H), 7.14 – 7.08 (m, 1H), 7.08 – 6.99 (m, 2H), 5.75 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.99, 163.94, 148.93, 144.02, 139.89, 136.69, 136.41, 130.18, 128.83, 128.47, 128.40, 128.04, 127.78, 127.51, 126.86, 122.09, 121.83, 71.95.

HRMS (ESI): $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}+\text{H}^+$ Calcd: 339.1492, Found: 339.1500.



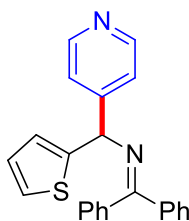
3k

N-(diphenylmethylene)-1-(furan-2-yl)-1-(pyridin-4-yl)methanamine (**3k**), 101.5mg, yield: 75%. White solid, mp 88-89°C.

^1H NMR (300 MHz, CDCl_3) δ 8.47 (d, $J = 5.9$ Hz, 2H), 7.65 (d, $J = 6.9$ Hz, 2H), 7.43 – 7.36 (m, 3H), 7.35 – 7.24 (m, 5H), 7.10 – 7.00 (m, 2H), 6.23 (dd, $J = 3.1$, 1.9 Hz, 1H), 6.05 (d, $J = 3.2$ Hz, 1H), 5.52 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 169.95, 154.82, 150.35, 149.90, 149.78, 142.25, 139.20, 135.93, 130.61, 128.87, 128.62, 128.12, 127.61, 122.69, 110.31, 107.06, 63.35.

HRMS (ESI): $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}+\text{H}^+$ Calcd: 339.1492, Found: 339.1500.



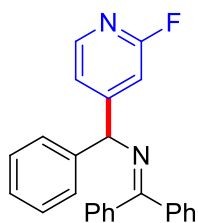
3l

N-(diphenylmethylene)-1-(pyridin-4-yl)-1-(thiophen-2-yl)methanamine (**3l**), 93.6mg, yield: 66%. White solid, mp 110-111°C.

^1H NMR (300 MHz, CDCl_3) δ 8.45 (d, $J = 5.2$ Hz, 2H), 7.68 (d, $J = 6.8$ Hz, 2H), 7.41 – 7.35 (m, 3H), 7.35 – 7.22 (m, 5H), 7.19 – 7.11 (m, 1H), 7.04 – 6.94 (m, 2H), 6.84 (dd, $J = 4.9$, 3.6 Hz, 1H), 6.71 (d, $J = 3.4$ Hz, 1H), 5.68 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 168.98, 152.97, 149.64, 146.82, 139.04, 135.78, 130.64, 130.03, 128.89, 128.61, 128.13, 127.48, 126.52, 125.09, 123.77, 122.31, 64.85.

HRMS (ESI): $\text{C}_{23}\text{H}_{18}\text{N}_2\text{S}+\text{H}^+$ Calcd: 355.1263, Found: 355.1269.



3m

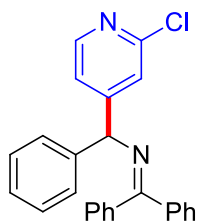
N-(diphenylmethylene)-1-(2-fluoropyridin-4-yl)-1-phenylmethanamine (**3m**), 99.7mg, yield: 68%. White solid, mp 106-107°C.

¹H NMR (300 MHz, CDCl₃) δ 8.09 (d, 1H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.51 – 7.43 (m, 3H), 7.40 (dd, *J* = 12.1, 7.4 Hz, 3H), 7.34 – 7.24 (m, 5H), 7.13 (d, *J* = 4.7 Hz, 1H), 6.96-7.04 (m, 3H), 5.51 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 168.77, 164.04 (d, *J*_{C-F} = 236.3 Hz) 159.65, 147.38 (d, *J*_{C-F} = 15.0 Hz) 142.70, 139.16, 136.12, 130.58, 128.85, 128.78, 128.72, 128.62, 128.14, 127.58, 127.53, 127.46, 120.24, 107.95 (d, *J*_{C-F} = 38.3 Hz) 68.66.

¹⁹F NMR (282 MHz, CDCl₃) δ -68.08.

HRMS (ESI): C₂₅H₁₉FN₂+H⁺ Calcd: 367.1605, Found: 367.1612.



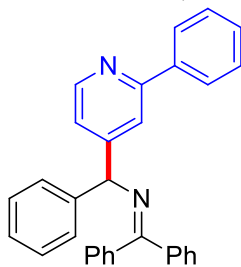
3n

1-(2-chloropyridin-4-yl)-*N*-(diphenylmethylene)-1-phenylmethanamine (**3n**), 107.2mg, yield: 70%. White solid, mp 117-118°C.

¹H NMR (300 MHz, CDCl₃) δ 8.26 (d, *J* = 5.1 Hz, 1H), 7.75 (d, *J* = 6.9 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.42 – 7.32 (m, 4H), 7.32 – 7.24 (m, 5H), 7.19 (d, *J* = 4.7 Hz, 1H), 7.07 – 6.99 (m, 2H), 5.48 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 168.79, 156.94, 151.56, 149.61, 149.46, 142.58, 139.06, 136.01, 130.60, 128.74, 128.62, 128.13, 127.54, 127.40, 122.80, 122.74, 121.32, 68.56.

HRMS (ESI): C₂₅H₁₉ClN₂+H⁺ Calcd: 383.1310, Found: 383.1316.



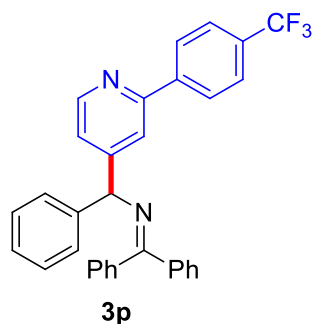
3o

N-(diphenylmethylene)-1-phenyl-1-(2-phenylpyridin-4-yl)methanamine (**3o**), 134.2mg, yield: 79%. Thick colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 8.50 (d, *J* = 5.1 Hz, 1H), 7.84 (d, *J* = 6.9 Hz, 2H), 7.68 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.61 (s, 1H), 7.40 – 7.33 (m, 4H), 7.33 – 7.21 (m, 8H), 7.19 – 7.10 (m, 3H), 7.03 – 6.93 (m, 2H), 5.49 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 168.29, 157.50, 154.28, 149.73, 149.62, 143.29, 139.52, 139.36, 136.32, 130.40, 128.77, 128.60, 128.09, 127.56, 127.26, 127.01, 126.92, 121.11, 119.43, 119.34, 69.21.

HRMS (ESI): C₃₁H₂₅N₂+H⁺ Calcd: 425.2012, Found: 425.2027.



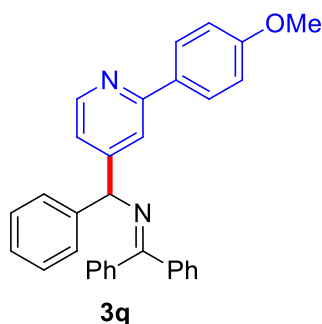
N-(diphenylmethylene)-1-phenyl-1-(2-(4-(trifluoromethyl)phenyl)pyridin-4-yl)methanamine (**3p**), 159.6mg, yield: 81%. Thick colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 8.53 (d, $J = 5.1$ Hz, 1H), 7.97 (d, $J = 8.1$ Hz, 2H), 7.71 – 7.59 (m, 5H), 7.43 – 7.36 (m, 3H), 7.36 – 7.26 (m, 4H), 7.25 – 7.13 (m, 5H), 7.03 – 6.94 (m, 2H), 5.51 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 168.62, 156.03, 154.75, 149.99, 143.23, 142.91, 139.39, 136.38, 130.57 (q, $J_{\text{C-F}} = 32.3$ Hz) 130.57, 128.87, 128.84, 128.74, 128.66, 128.21, 127.64, 127.61, 127.45, 127.33, 126.62 (q, $J_{\text{C-F}} = 32.3$ Hz) 122.01, 119.76, 69.16.

^{19}F NMR (282 MHz, CDCl_3) δ -62.50.

HRMS (ESI): $\text{C}_{32}\text{H}_{23}\text{F}_3\text{N}_2 + \text{H}^+$ Calcd: 493.1886, Found: 493.1902.

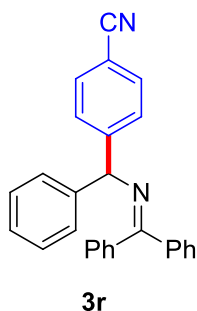


N-(diphenylmethylene)-1-(2-(4-methoxyphenyl)pyridin-4-yl)-1-phenylmethanamine (**3q**), 138.2mg, yield: 76%. Thick colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 8.46 (d, $J = 5.0$ Hz, 1H), 7.81 (d, $J = 8.8$ Hz, 2H), 7.68 (d, $J = 6.6$ Hz, 2H), 7.55 (s, 1H), 7.40 – 7.33 (m, 3H), 7.31 – 7.18 (m, 7H), 7.16 – 7.09 (m, 2H), 7.03 – 6.95 (m, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.47 (s, 1H), 3.74 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 168.25, 160.33, 157.14, 154.18, 149.52, 143.36, 139.43, 136.38, 132.14, 130.39, 128.78, 128.73, 128.59, 128.55, 128.23, 128.10, 127.60, 127.24, 120.49, 118.63, 113.99, 69.21, 55.31.

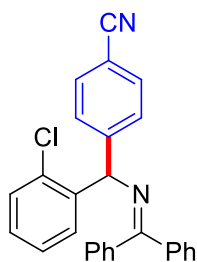
HRMS (ESI): $\text{C}_{32}\text{H}_{26}\text{N}_2\text{O} + \text{H}^+$ Calcd: 455.2118, Found: 455.2134.



4-(((diphenylmethylene)amino)(phenyl)methyl)benzonitrile (**3r**), 98.3mg, yield: 66%. Thick colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 7.74 (d, $J = 6.9$ Hz, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.49 – 7.44 (m, 5H), 7.39 – 7.35 (m, 2H), 7.34 – 7.27 (m, 5H), 7.08 – 6.99 (m, 2H), 5.57 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 168.14, 150.20, 143.56, 139.32, 136.29, 132.22, 130.45, 128.75, 128.61, 128.56, 128.45, 128.19, 128.10, 127.49, 127.48, 127.23, 119.01, 110.44, 69.45.
HRMS (ESI): $\text{C}_{27}\text{H}_{20}\text{N}_2+\text{H}^+$ Calcd: 373.1699, Found: 373.1696.



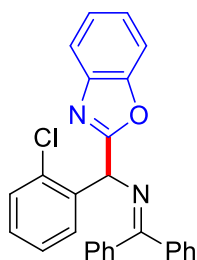
3s

4-((2-chlorophenyl)((diphenylmethylene)amino)methyl)benzonitrile (**3s**), 114.0mg, yield: 70%. Thick colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 7.80 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.70 – 7.62 (m, 2H), 7.52 – 7.45 (m, 2H), 7.43 – 7.37 (m, 4H), 7.36 – 7.24 (m, 4H), 7.23 – 7.17 (m, 2H), 7.15 – 7.06 (m, 1H), 6.97 – 6.87 (m, 2H), 6.01 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 169.11, 148.98, 141.16, 139.24, 136.28, 132.37, 132.18, 130.58, 129.94, 129.48, 128.82, 128.63, 128.37, 128.30, 128.13, 127.38, 127.33, 118.99, 110.55, 65.13.

HRMS (ESI): $\text{C}_{27}\text{H}_{20}\text{ClN}_2+\text{H}^+$ Calcd: 407.1310, Found: 407.1309.



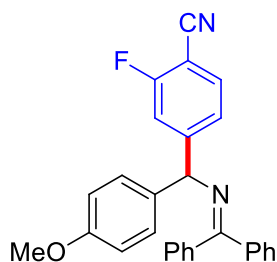
3t

1-(benzo[d]oxazol-2-yl)-1-(2-chlorophenyl)-*N*-(diphenylmethylene)methanamine (**3t**), 90.1mg, yield: 58%. Thick colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 7.96 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.71 – 7.60 (m, 3H), 7.43 – 7.36 (m, 4H), 7.35 – 7.28 (m, 3H), 7.27 – 7.19 (m, 5H), 7.13 – 7.04 (m, 2H), 6.31 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 171.75, 165.29, 150.93, 141.20, 139.17, 137.39, 135.88, 132.95, 130.76, 130.53, 129.40, 129.17, 129.05, 129.02, 128.72, 128.10, 127.64, 127.25, 124.86, 124.14, 120.39, 110.74, 61.23.

HRMS (ESI): $\text{C}_{27}\text{H}_{20}\text{ClN}_2\text{O}+\text{H}^+$ Calcd: 423.1259, Found: 423.1258.



3u

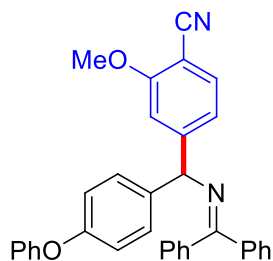
4-(((diphenylmethylene)amino)(4-methoxyphenyl)methyl)-2-fluorobenzonitrile (**3u**), 58.9 mg, yield: 35%. Thick colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 7.74 (dd, $J = 8.1, 1.5$ Hz, 2H), 7.46 (dd, $J = 5.6, 2.4$ Hz, 4H), 7.42 – 7.28 (m, 5H), 7.26 – 7.21 (m, 2H), 7.11 – 6.90 (m, 9H), 5.52 (s, 1H), 3.88 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 168.33, 163.25 (d, $J_{\text{C-F}} = 256.9$ Hz) 158.88, 153.95 (d, $J_{\text{C-F}} = 7.3$ Hz) 139.19, 136.18, 135.24, 133.24, 130.58, 128.84, 128.76, 128.63, 128.56, 128.16, 127.46, 123.66 (d, $J_{\text{C-F}} = 3.27$ Hz) 115.23 (d, $J_{\text{C-F}} = 20.2$ Hz), 114.24, 114.11, 99.28 (d, $J_{\text{C-F}} = 15.65$ Hz), 68.49, 55.26.

^{19}F NMR (282 MHz, CDCl_3) -106.24

HRMS (ESI): $\text{C}_{28}\text{H}_{21}\text{FN}_2\text{O} + \text{Na}^+$ Calcd: 443.1530, Found: 443.1513.



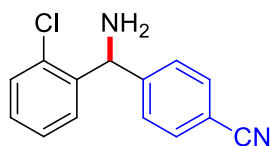
3v

4-(((diphenylmethylene)amino)(4-phenoxyphenyl)methyl)-2-methoxybenzonitrile (**3v**), 134.5mg, yield: 68%. Thick colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 7.74 (dd, $J = 8.1, 1.5$ Hz, 2H), 7.46 (dd, $J = 5.6, 2.4$ Hz, 4H), 7.42 – 7.28 (m, 5H), 7.26 – 7.21 (m, 2H), 7.11 – 6.90 (m, 9H), 5.52 (s, 1H), 3.88 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 168.18, 161.42, 156.99, 156.44, 152.24, 139.37, 138.36, 136.33, 133.69, 130.54, 130.09, 129.77, 128.85, 128.76, 08, 55.98.

HRMS (ESI): $\text{C}_{34}\text{H}_{26}\text{N}_2\text{O}_2 + \text{H}^+$ Calcd: 495.2067, Found: 495.2049.



4

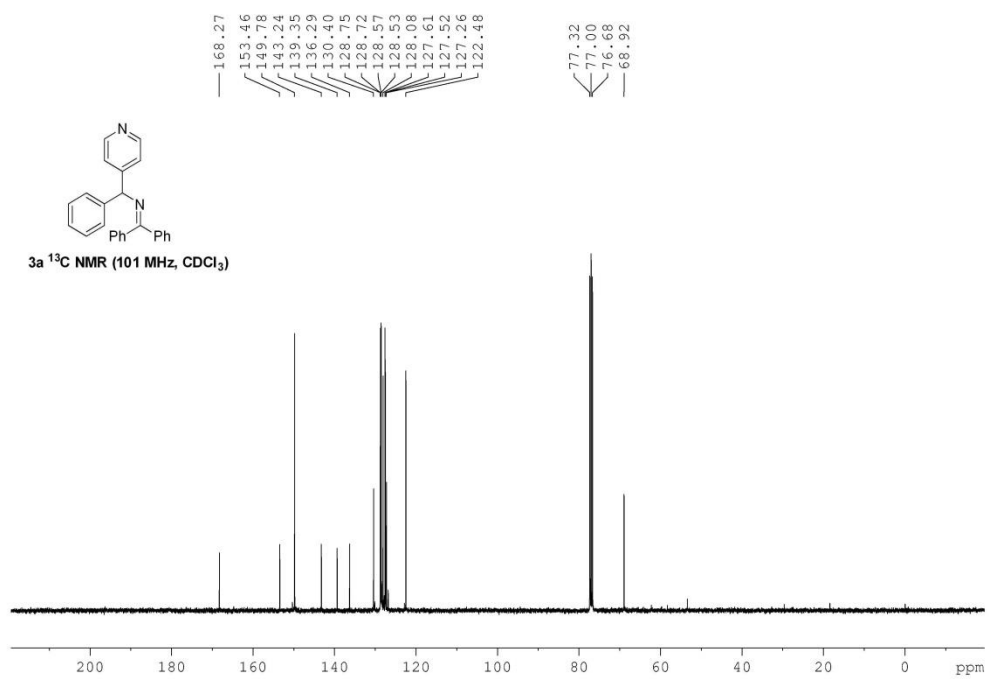
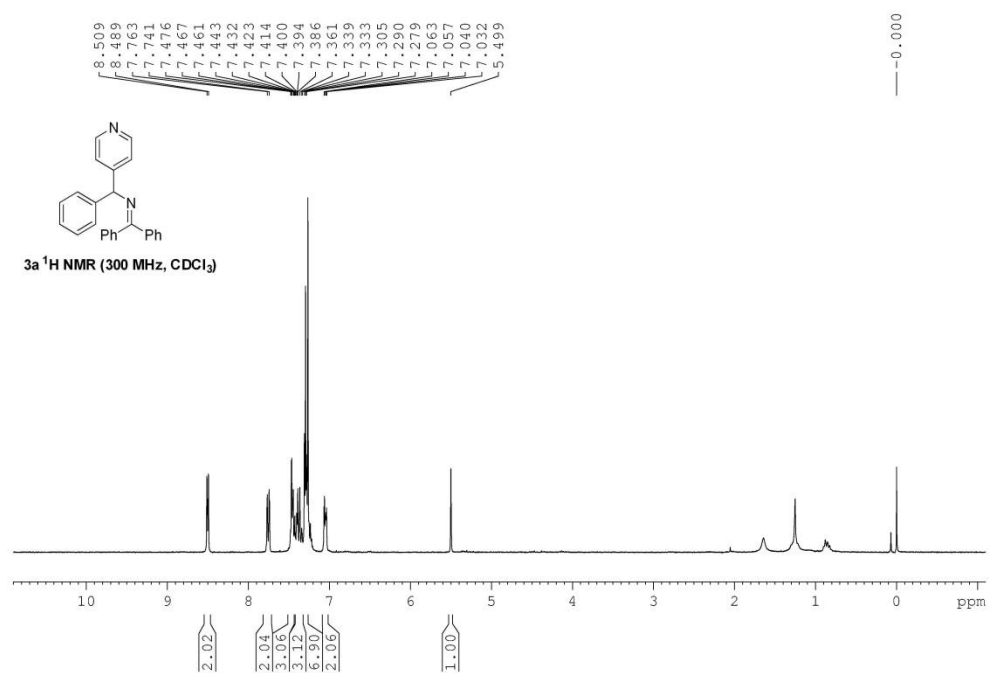
4-(amino(2-chlorophenyl)methyl)benzonitrile (**4**), 23.3mg, yield: 96%. Thick colorless oil.

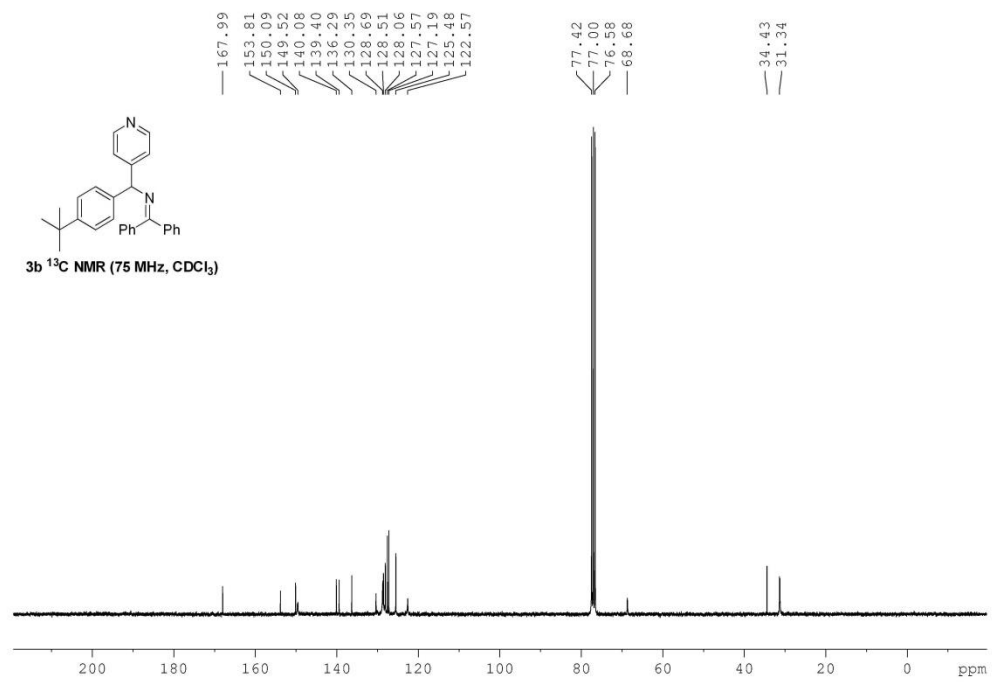
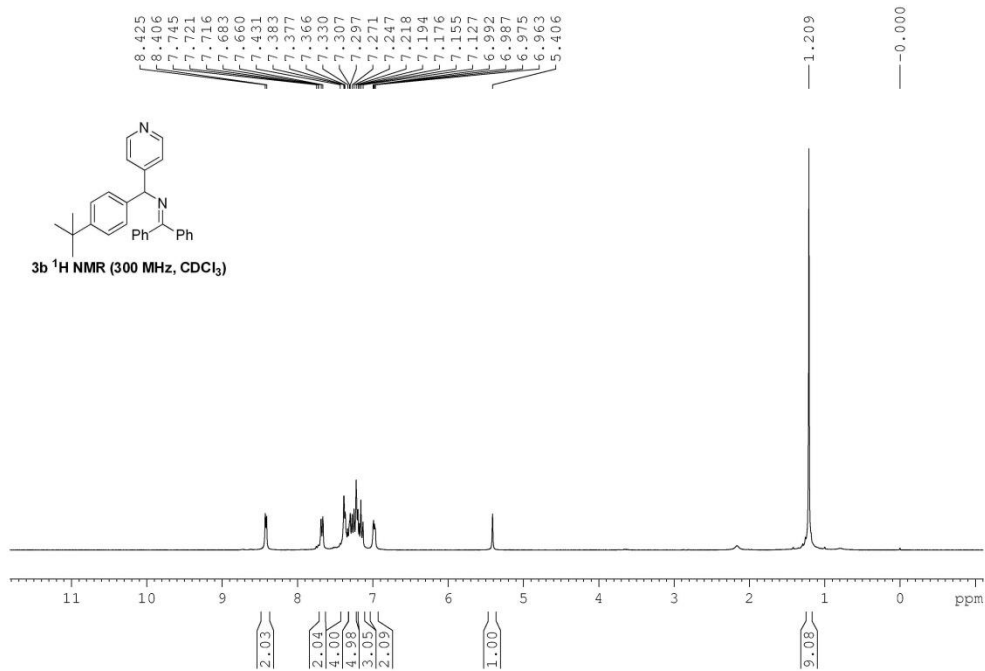
^1H NMR (300 MHz, CDCl_3) δ 7.53 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.39 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.29 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.22 (dd, $J = 7.4, 1.6$ Hz, 1H), 7.19 – 7.11 (m, 1H), 5.61 (s, 1H), 1.93 (s, 2H).

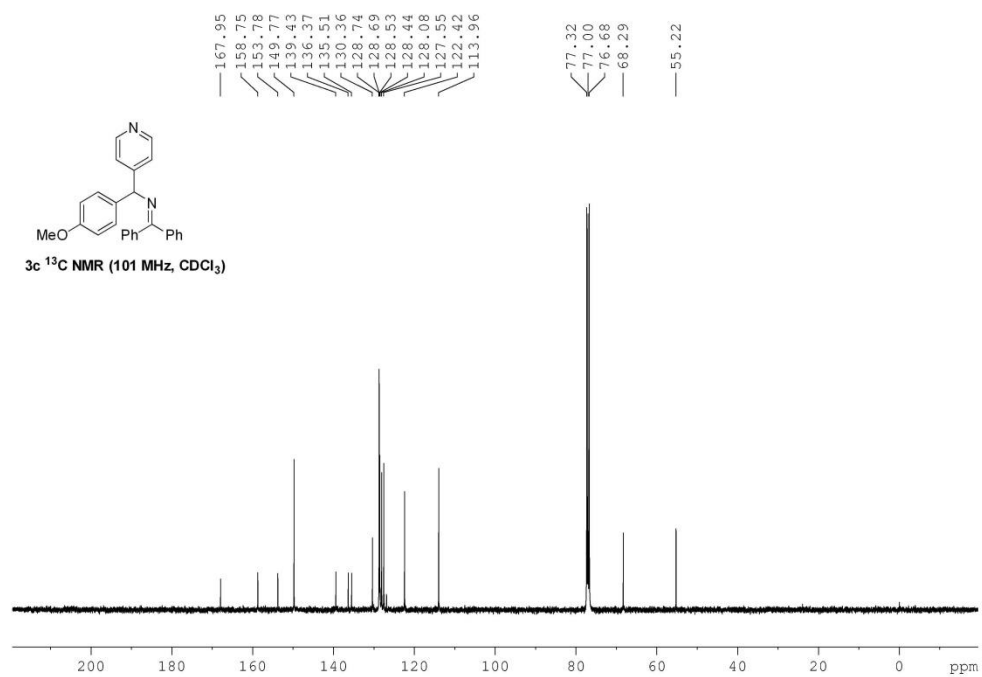
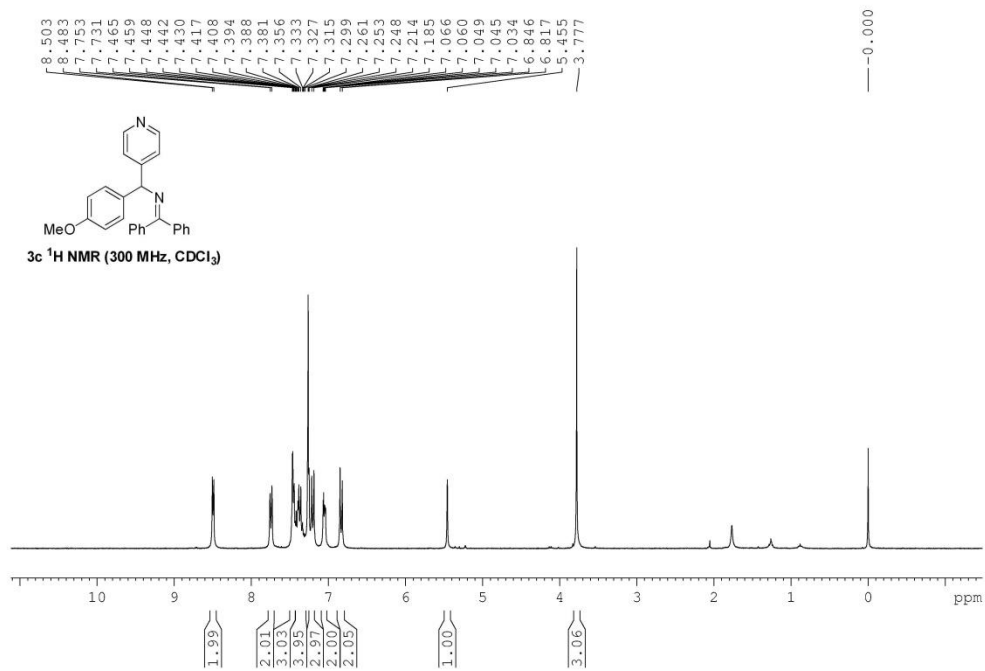
^{13}C NMR (75 MHz, DMSO) δ 149.36, 141.25, 132.29, 131.88, 129.39, 128.92, 128.63, 128.29, 127.57, 118.82, 109.70, 55.19.

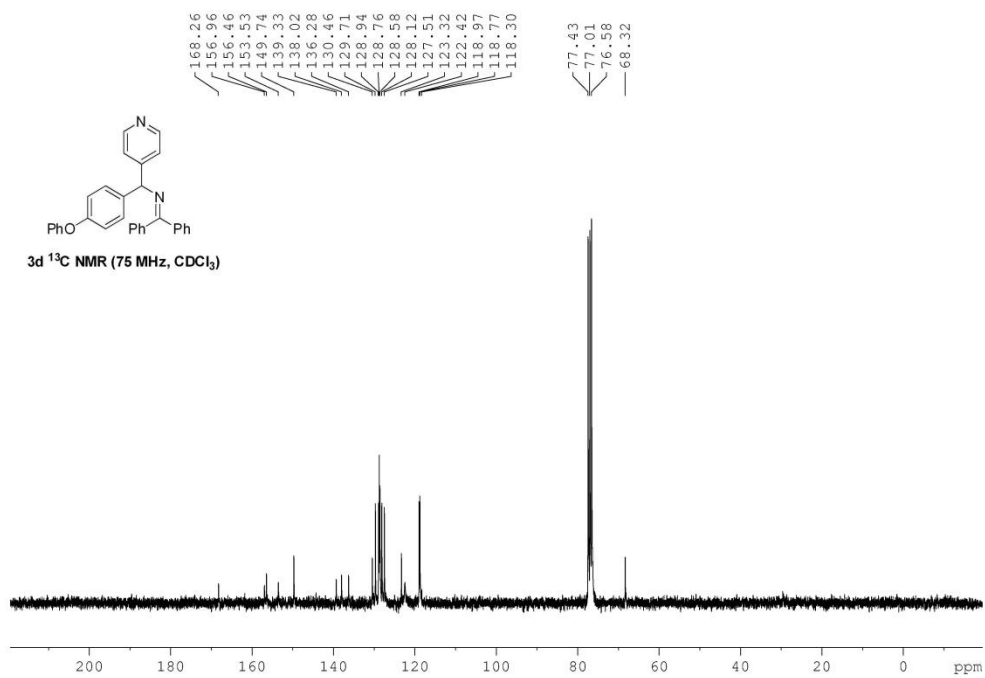
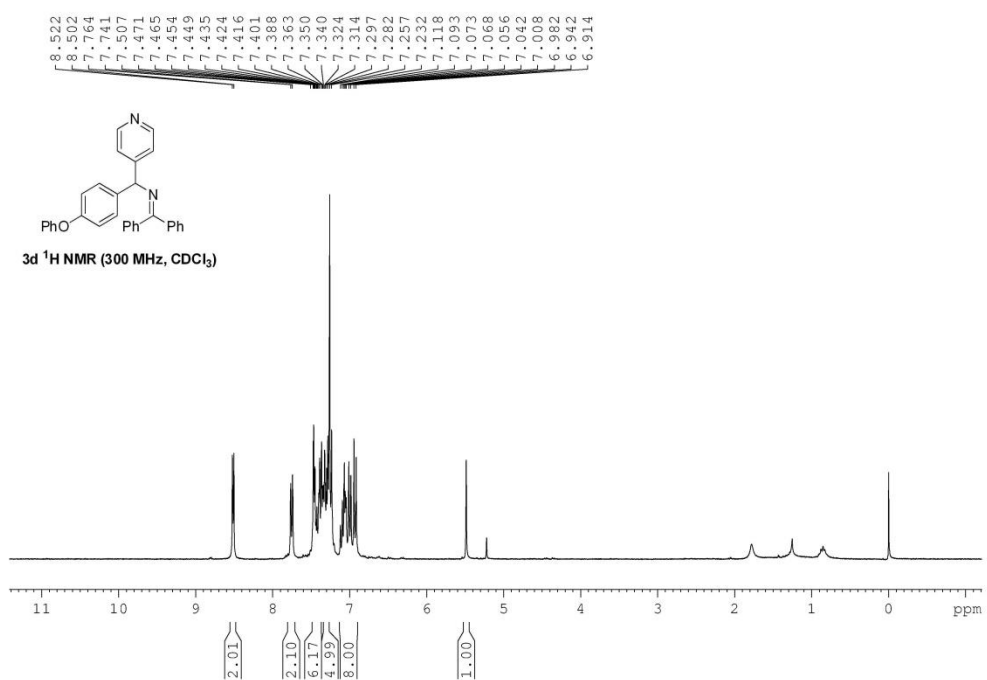
HRMS (ESI): $\text{C}_{14}\text{H}_{11}\text{ClN}_2 + \text{H}^+$ Calcd: 243.0684, Found: 243.0682.

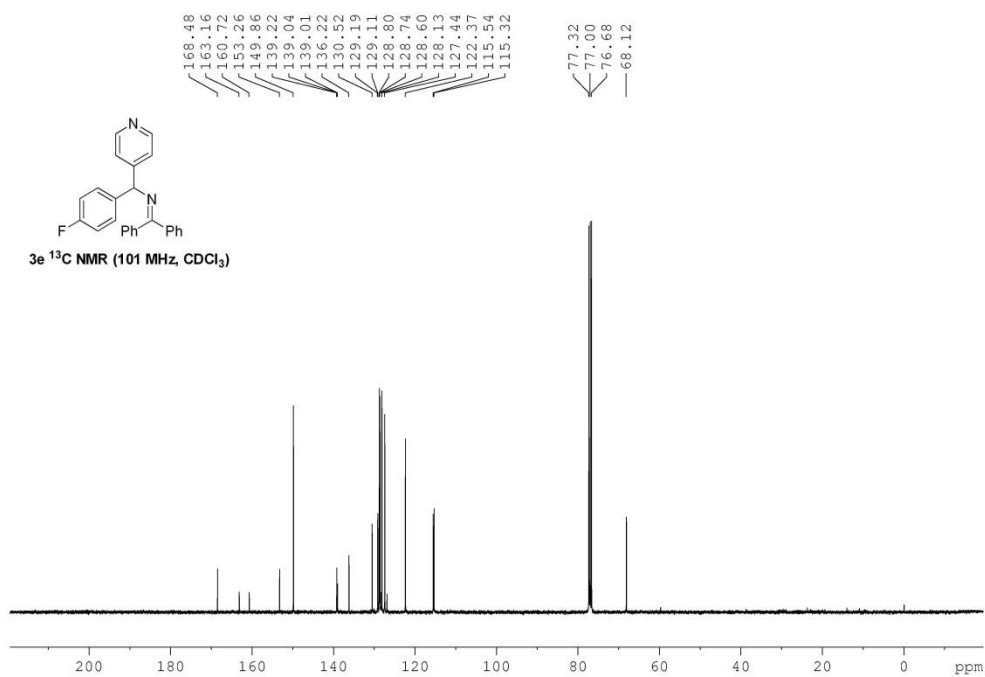
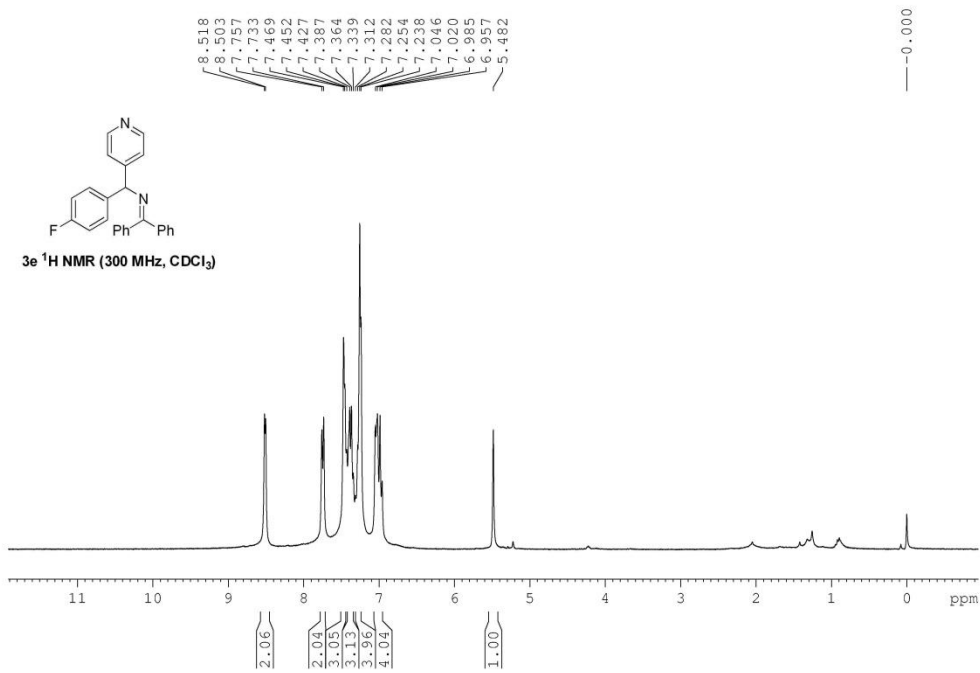
9. NMR spectra of new compounds

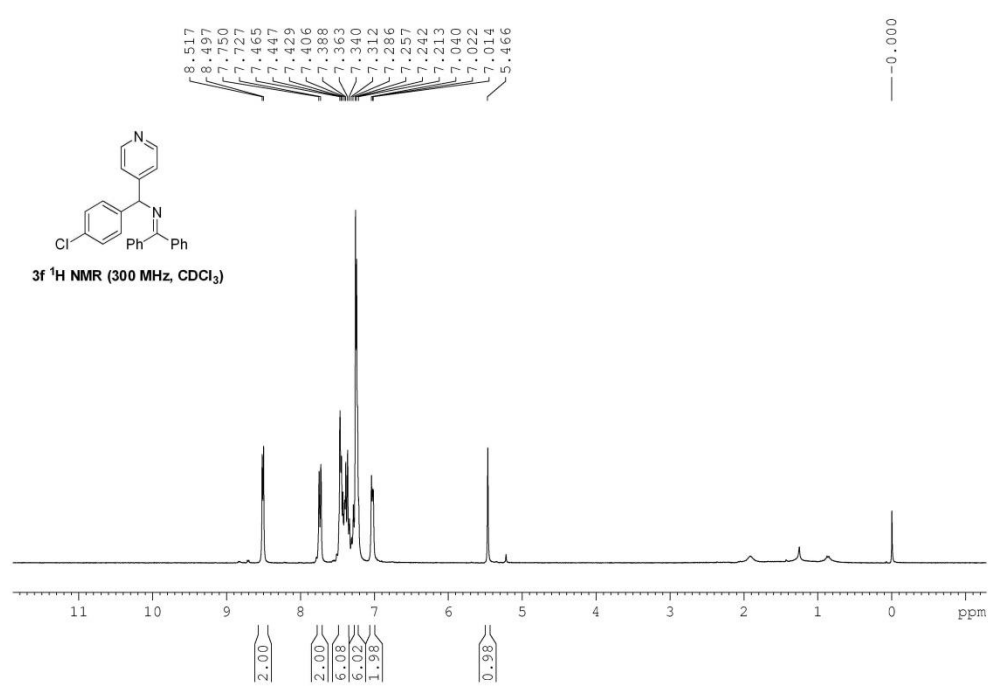
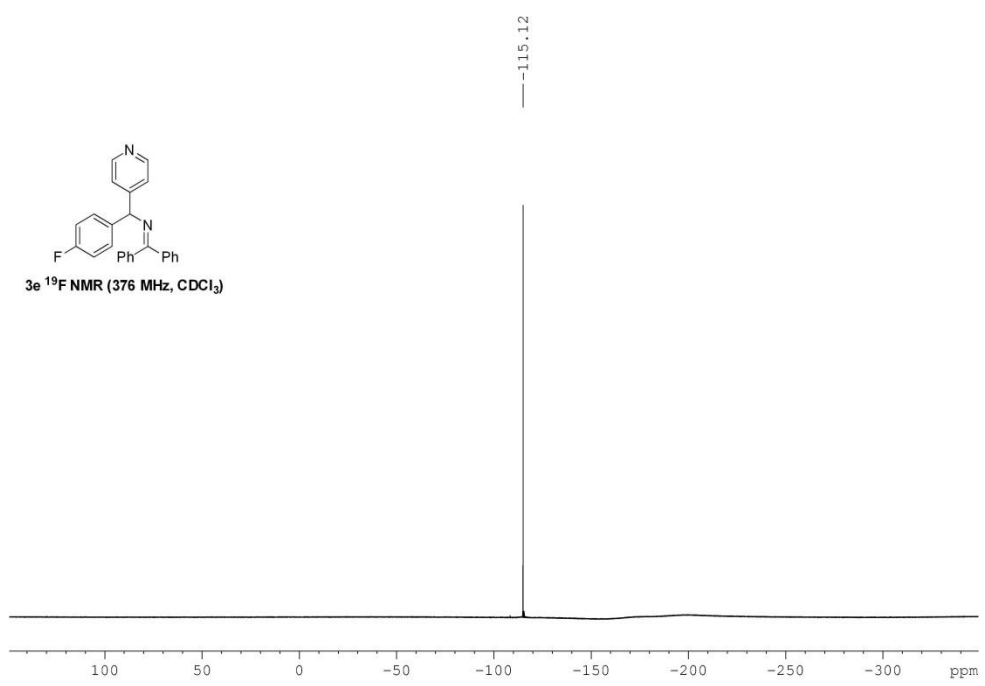


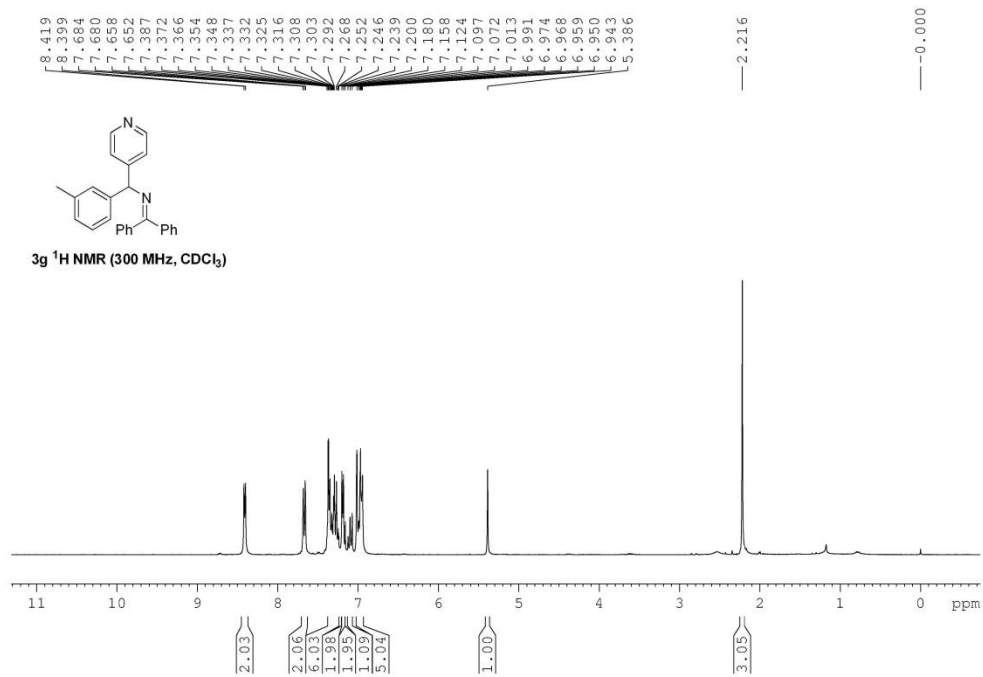
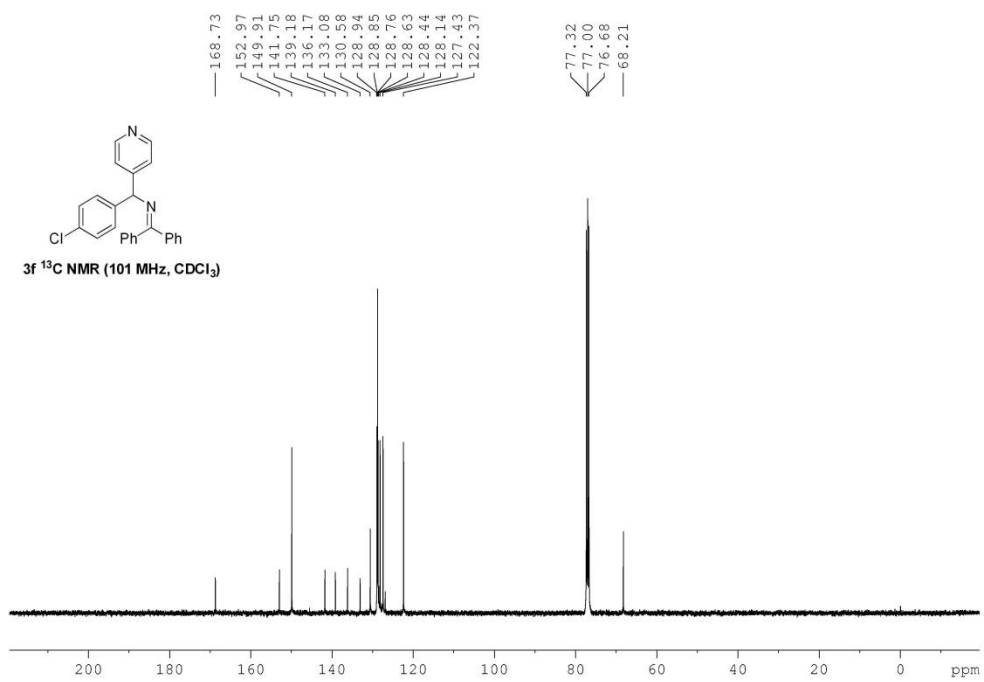


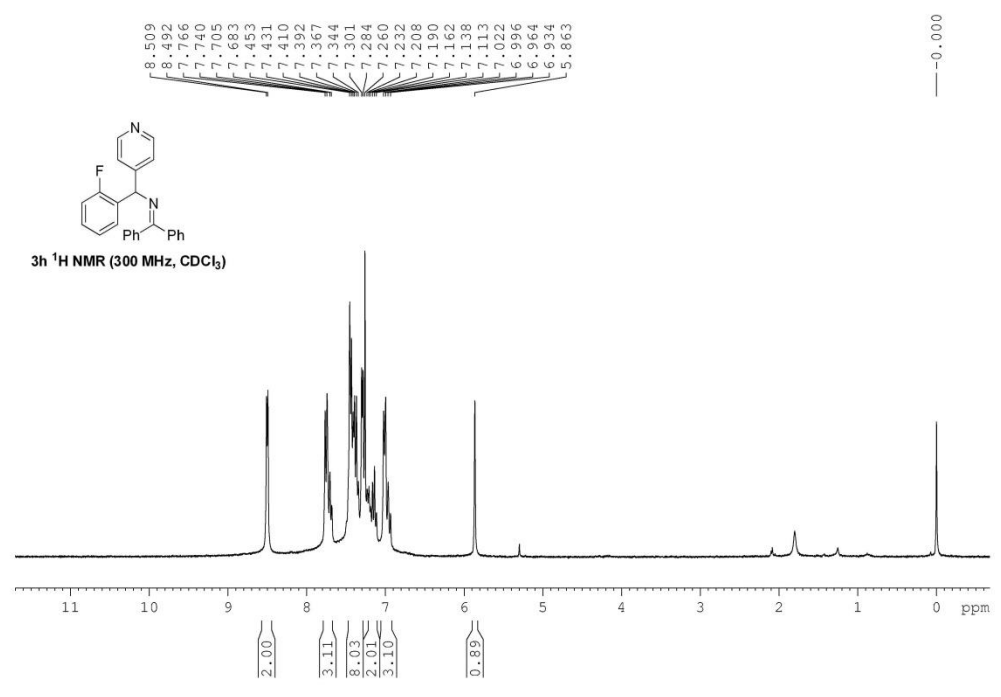
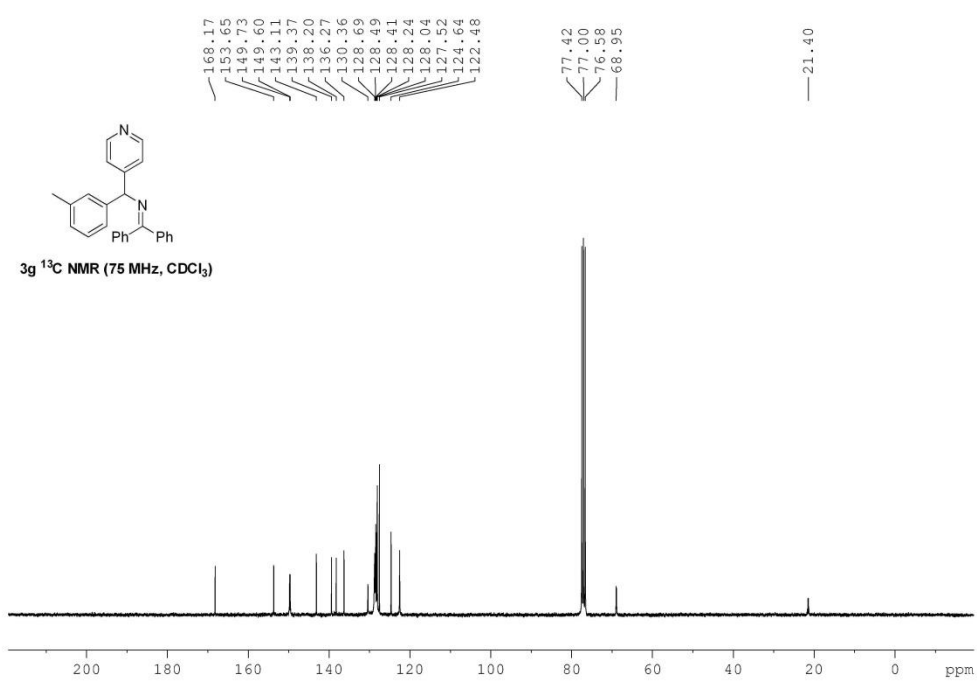


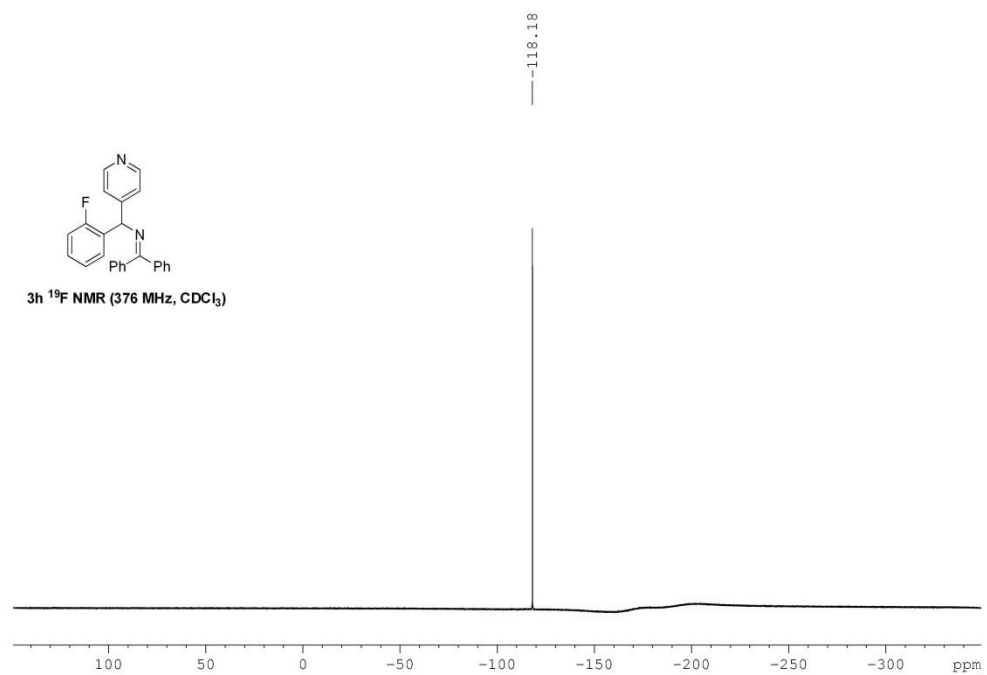
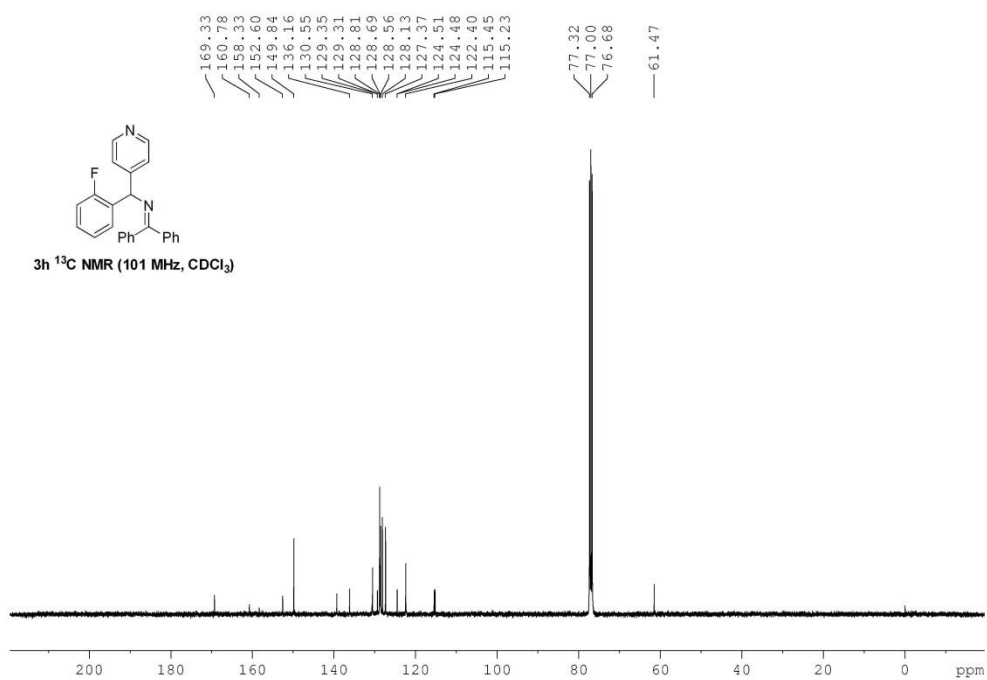


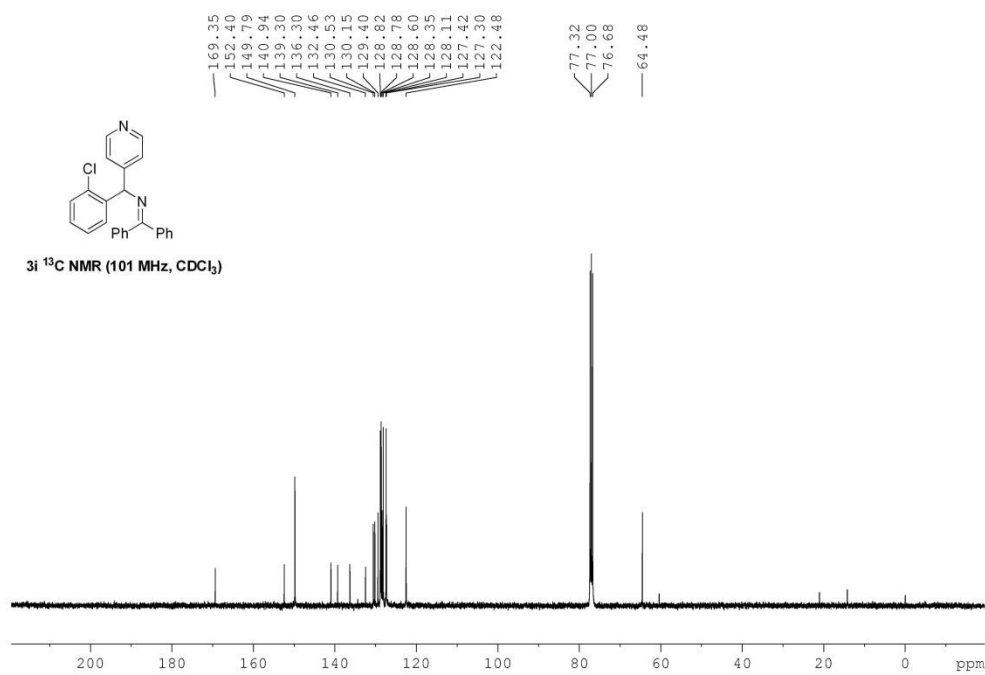
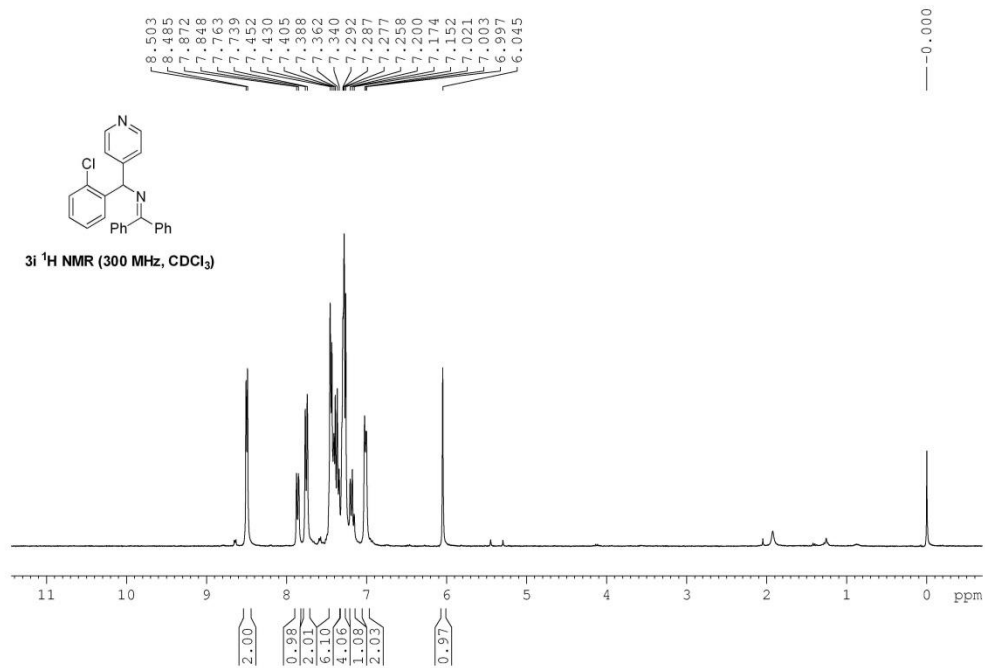


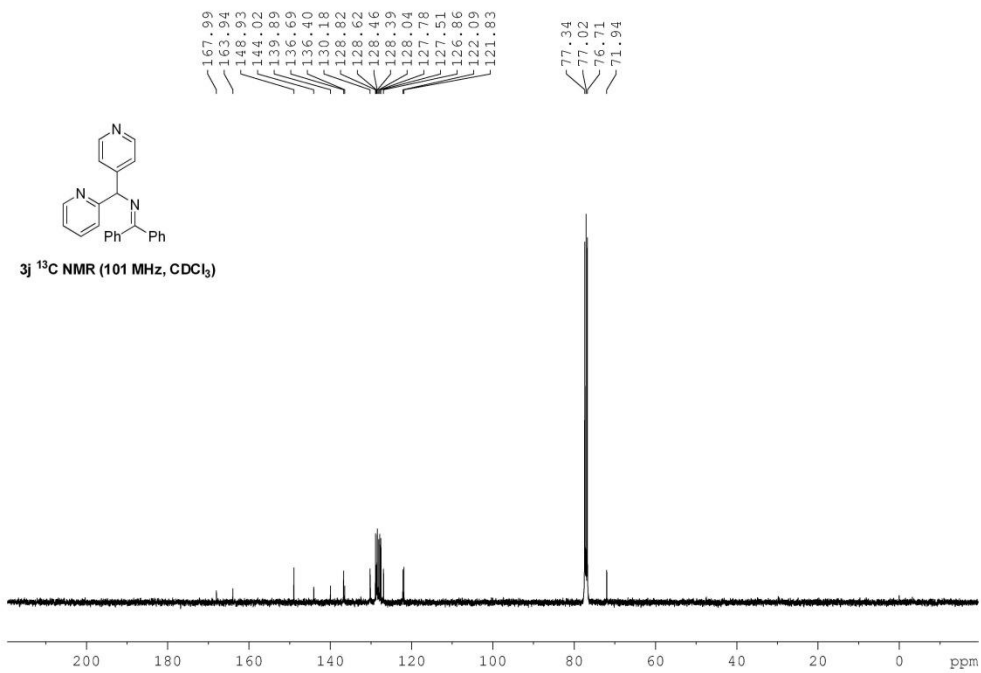
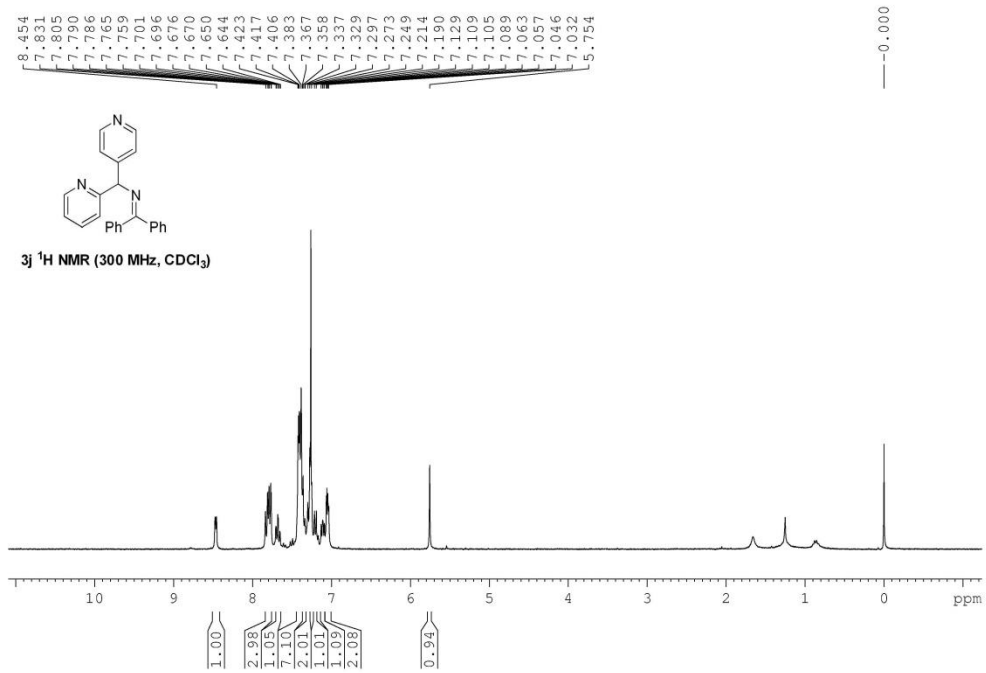


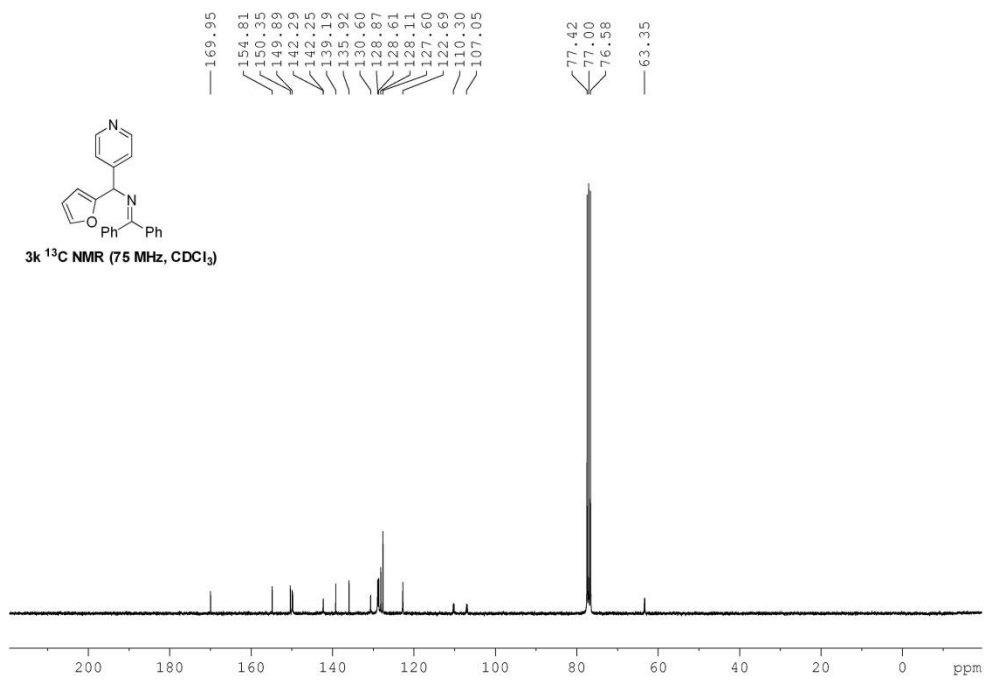
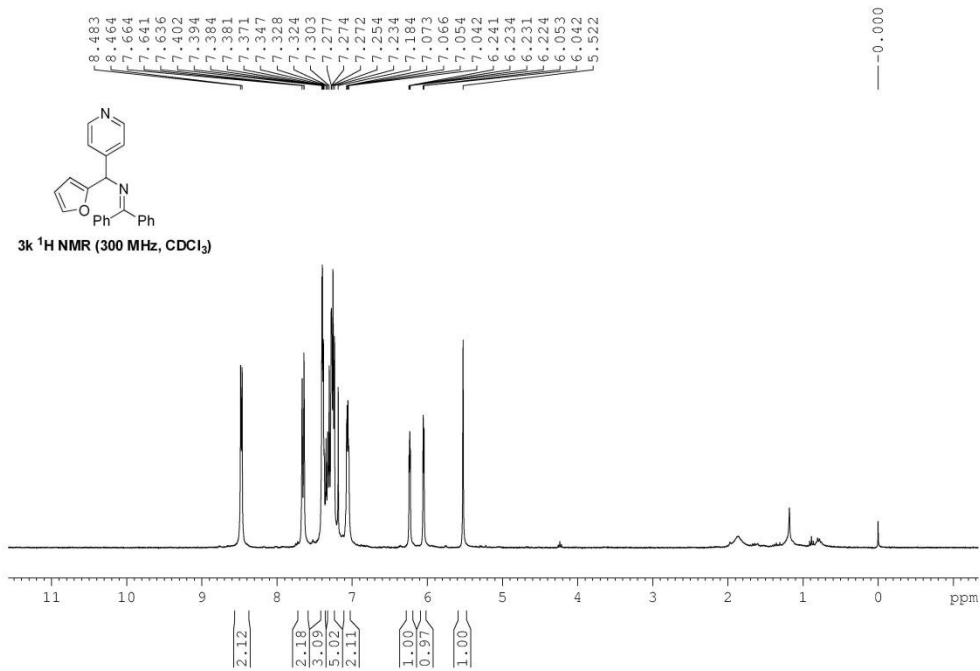


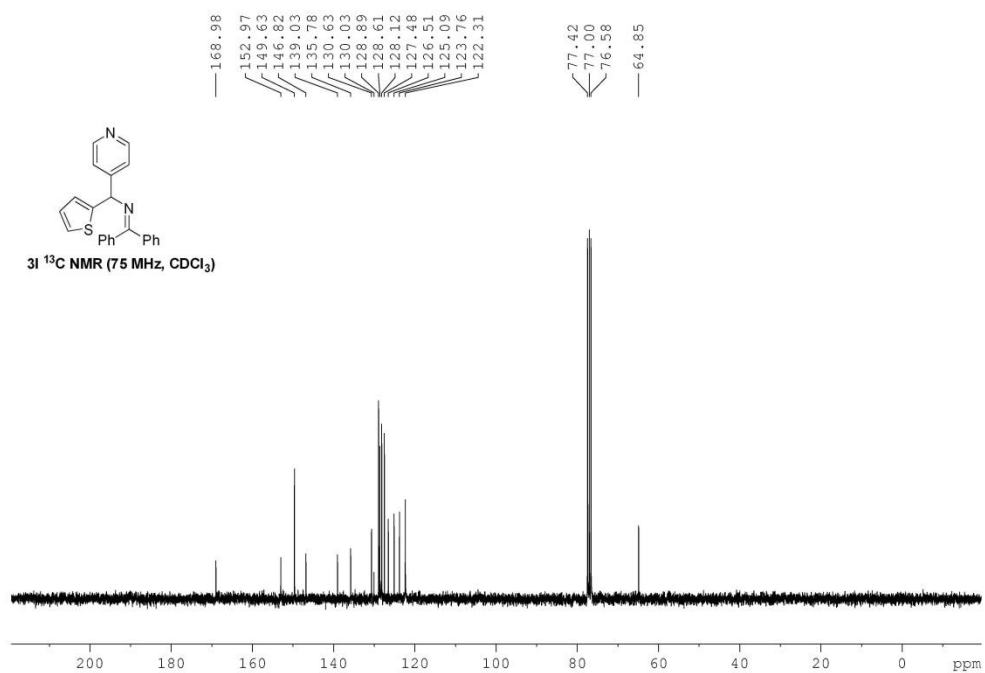
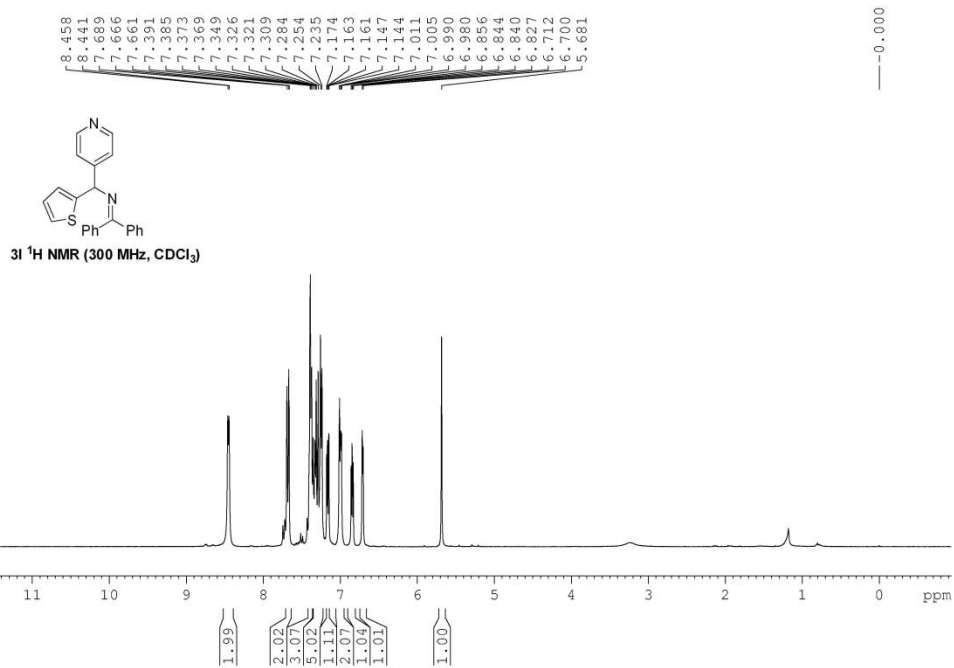


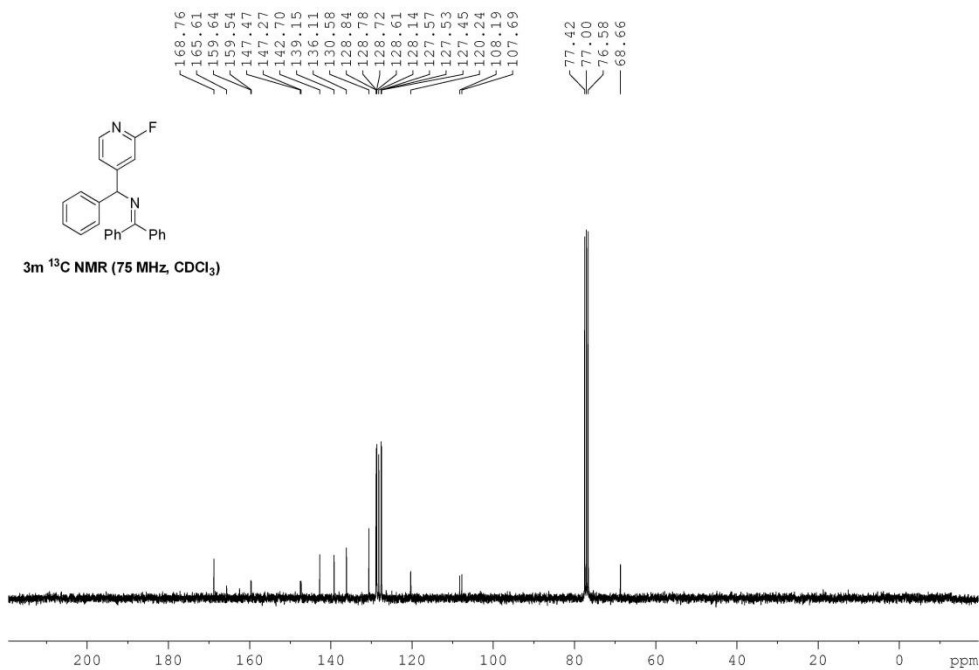
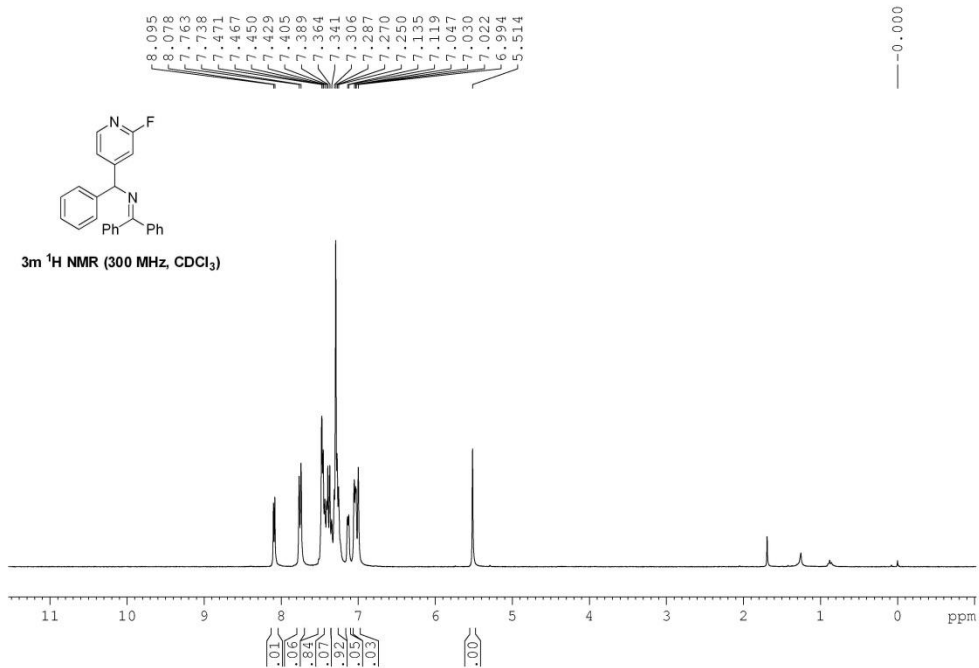


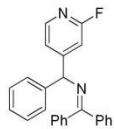




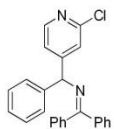
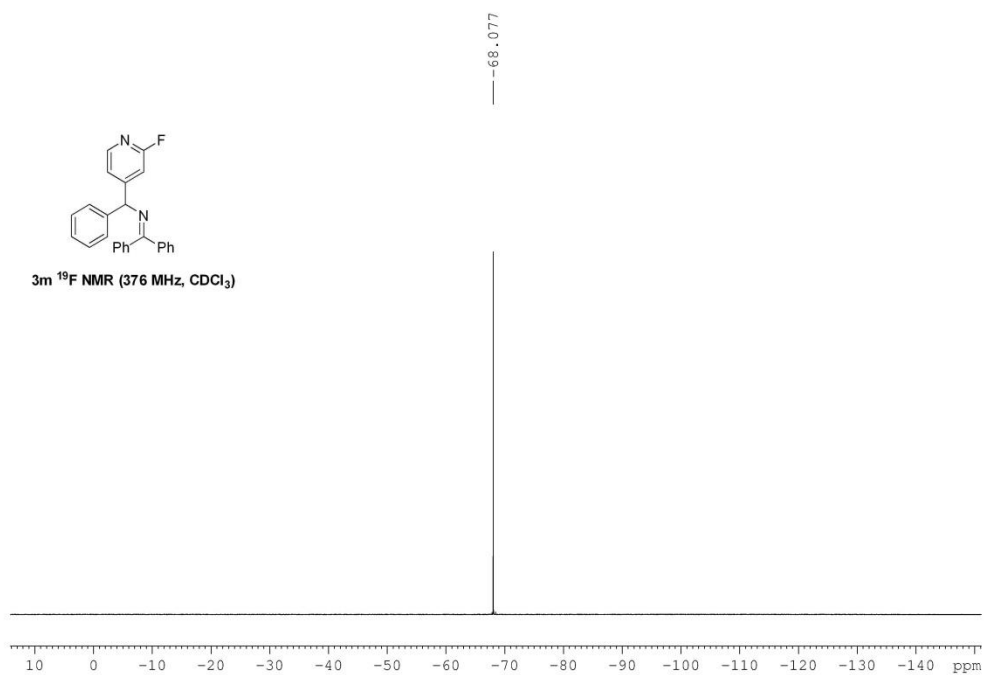




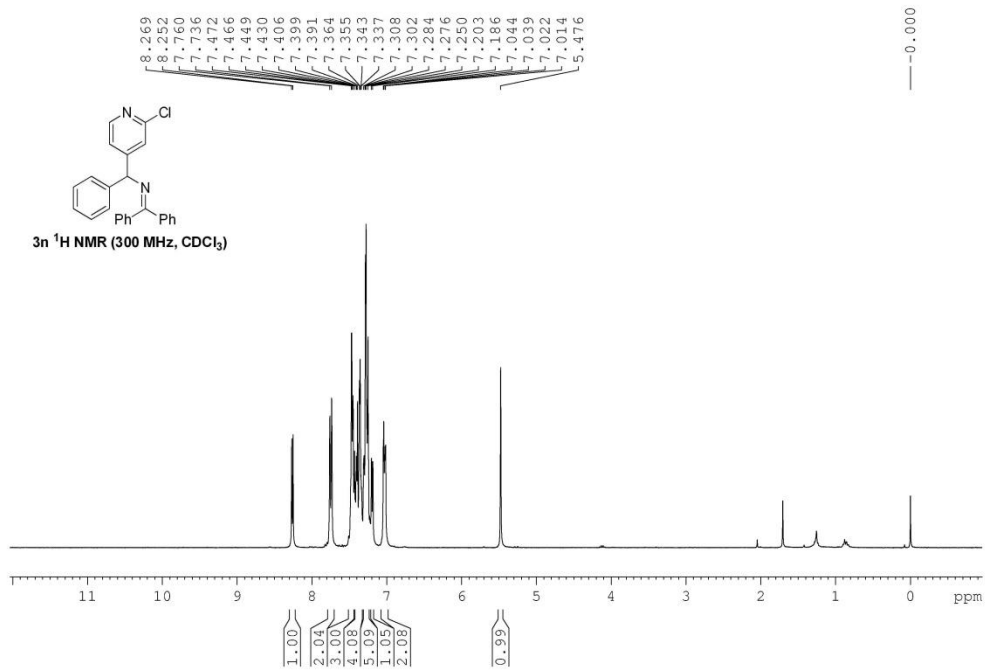


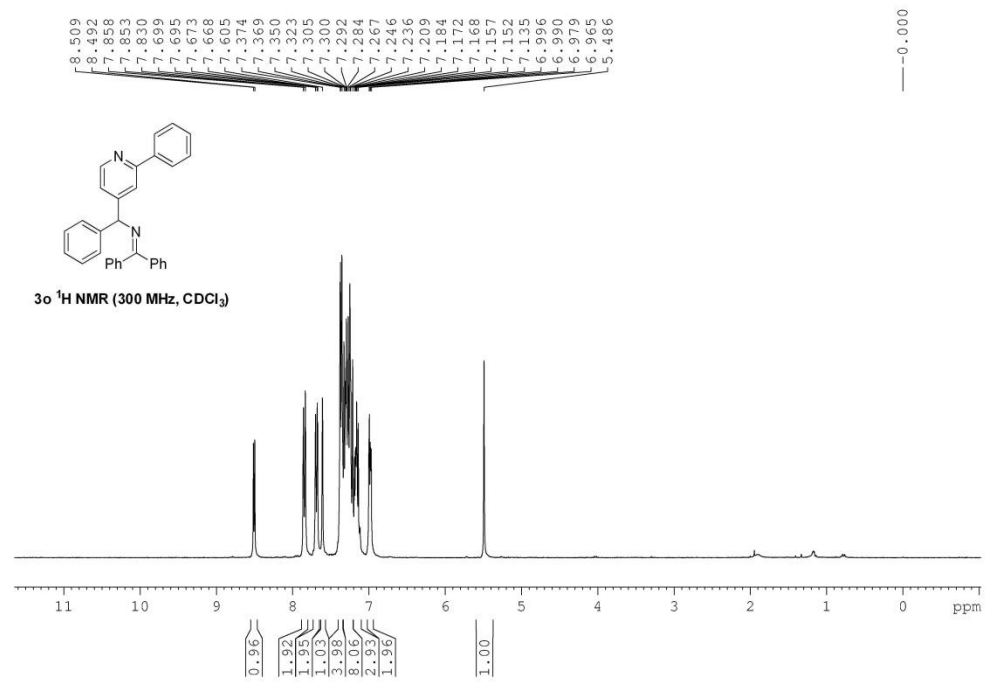
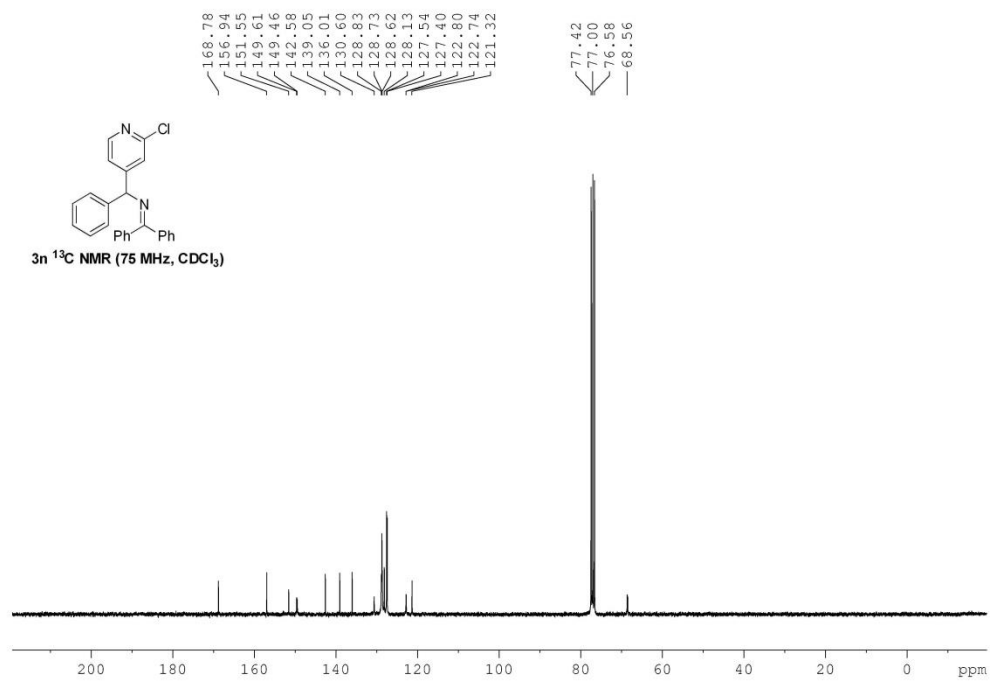


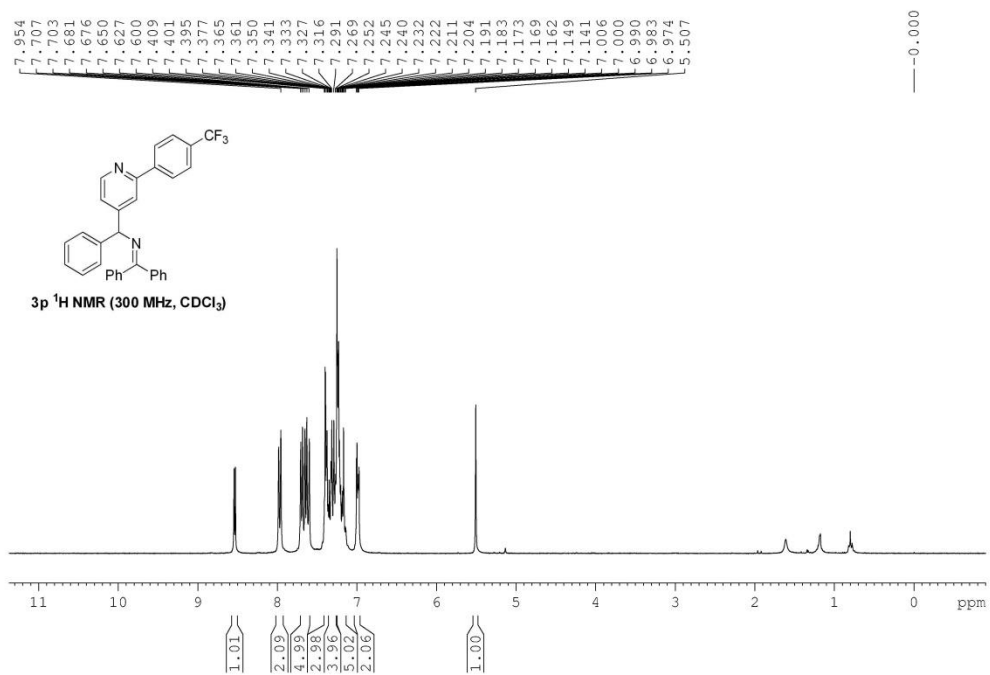
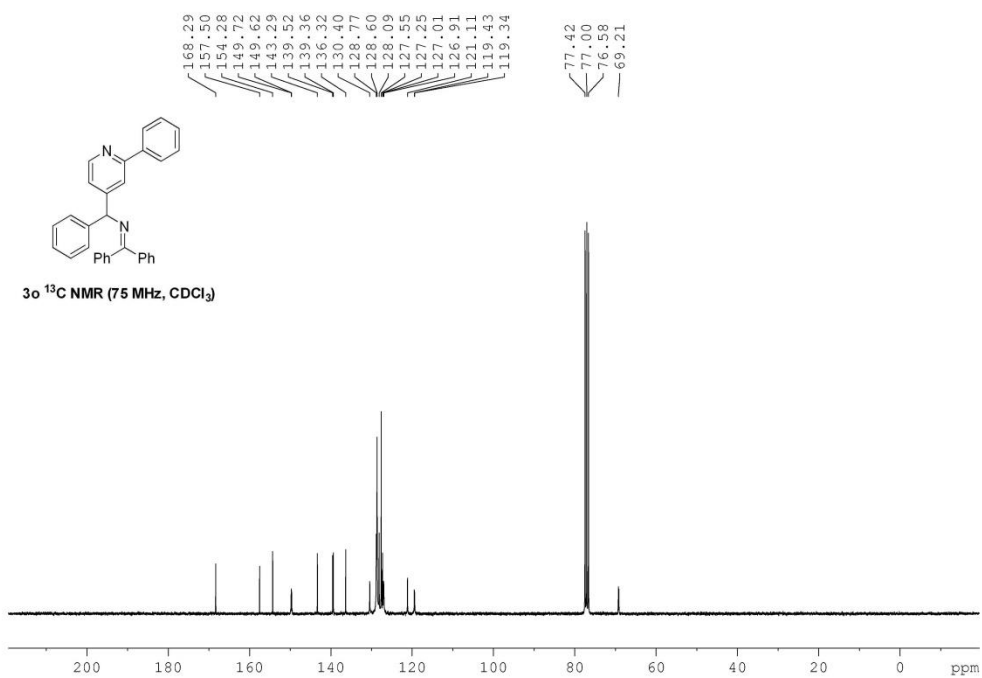
3m ¹⁹F NMR (376 MHz, CDCl₃)

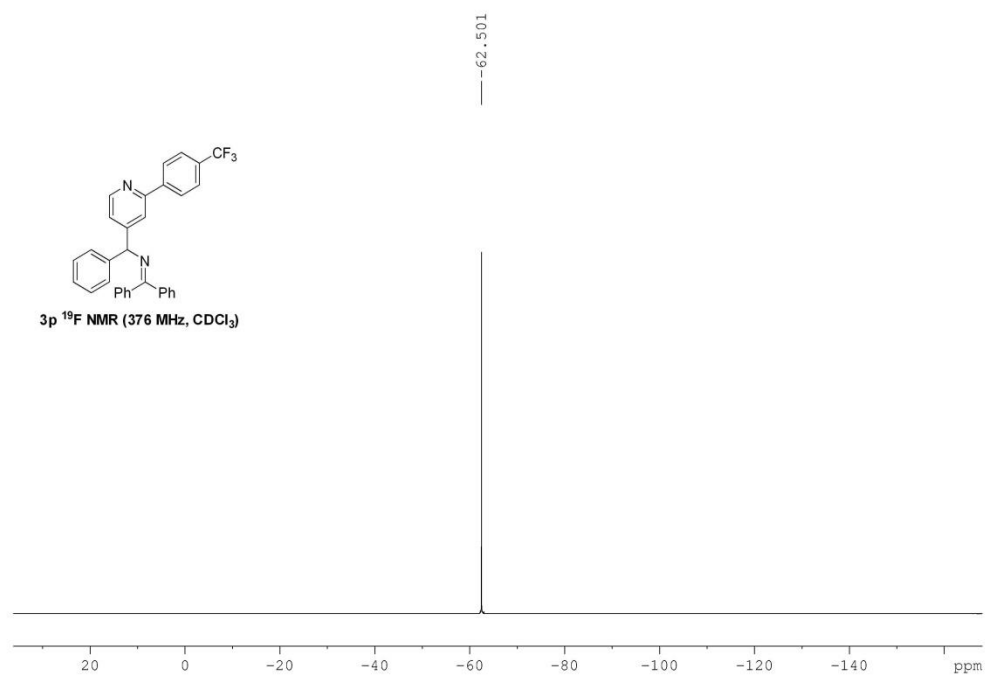
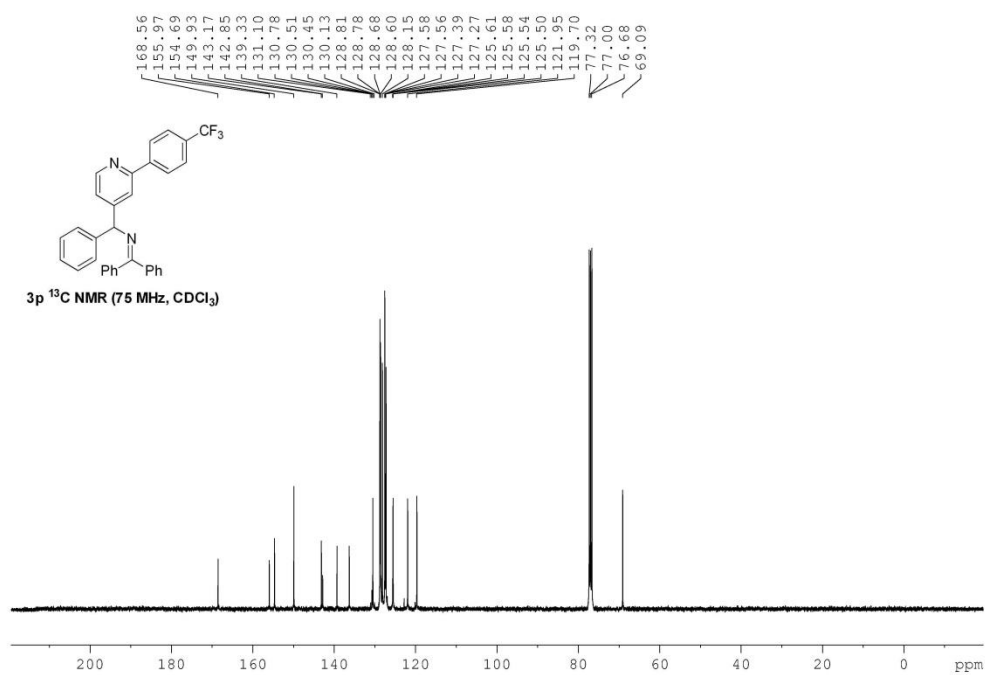


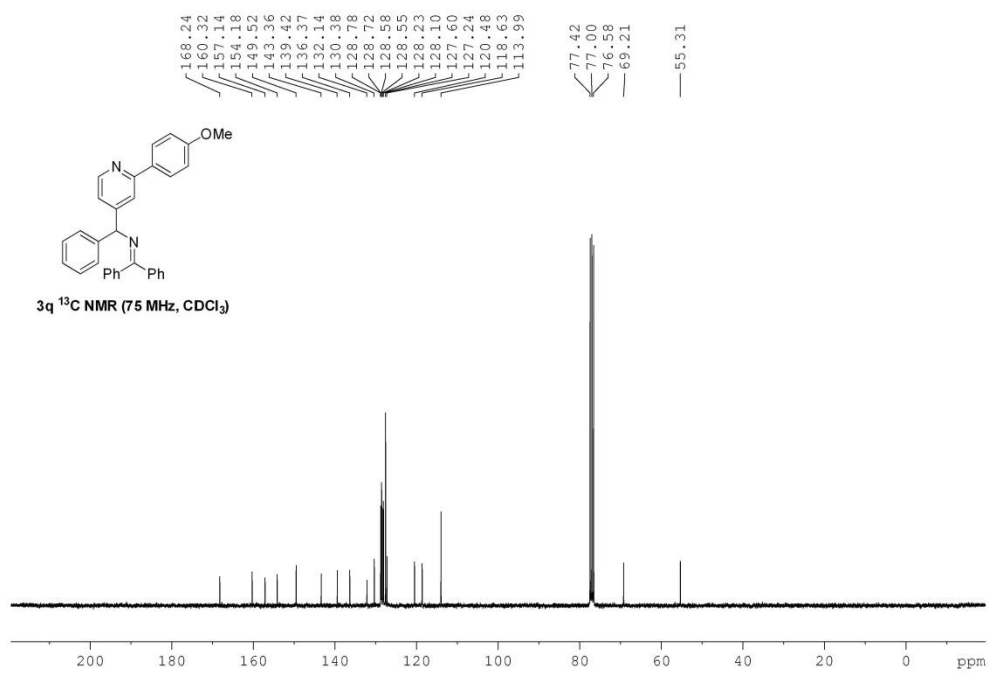
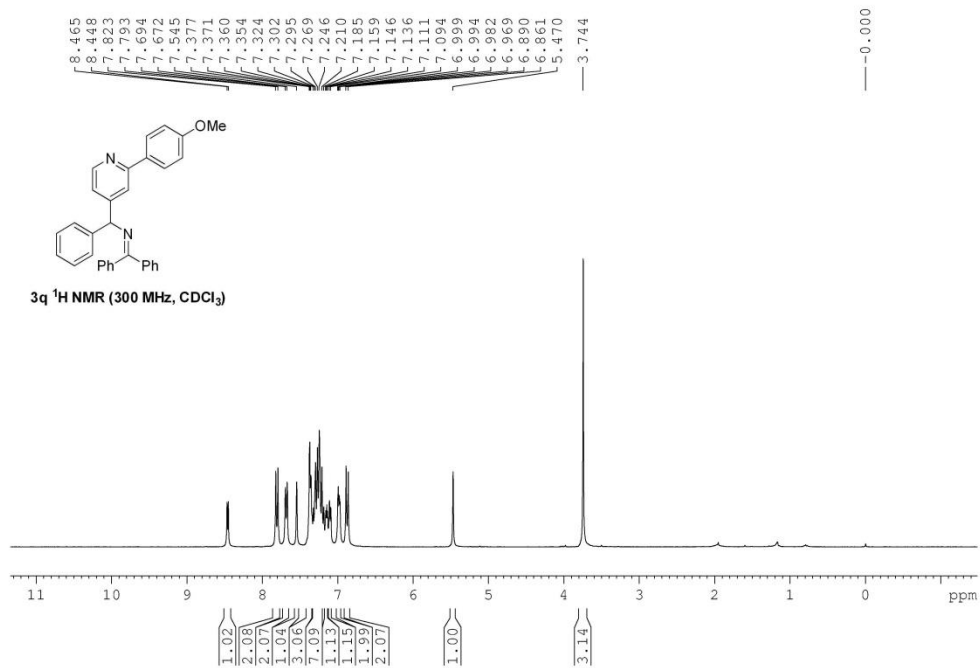
3n ¹H NMR (300 MHz, CDCl₃)

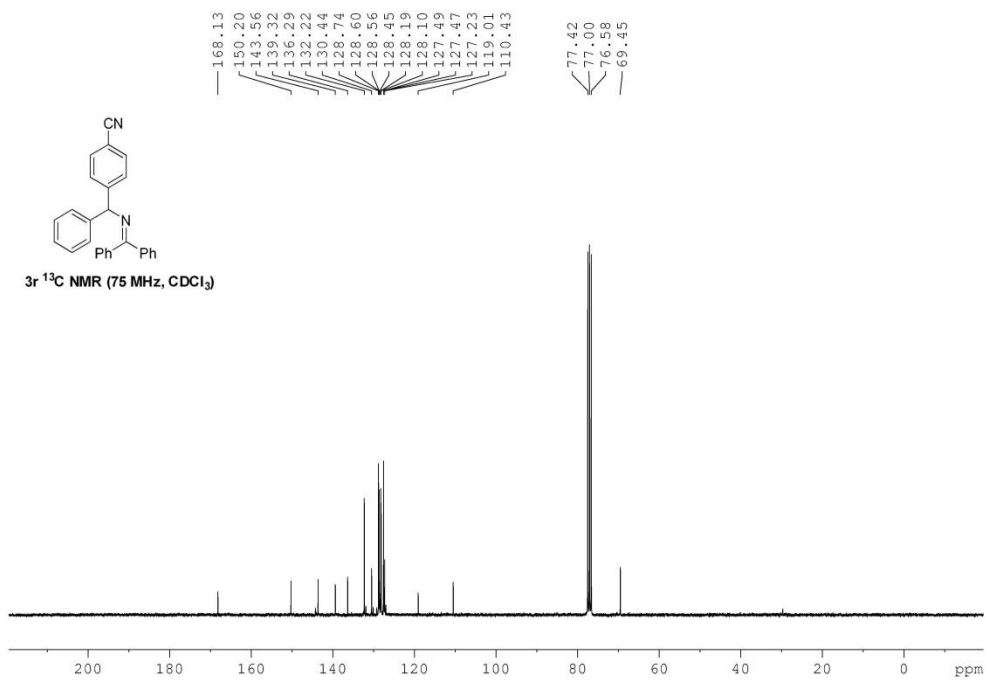
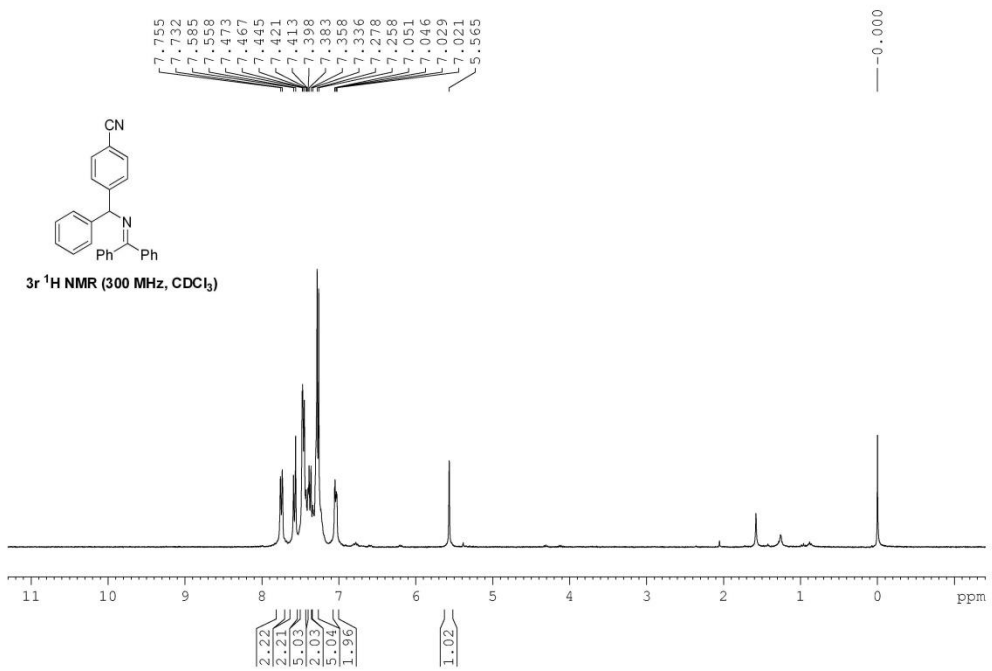


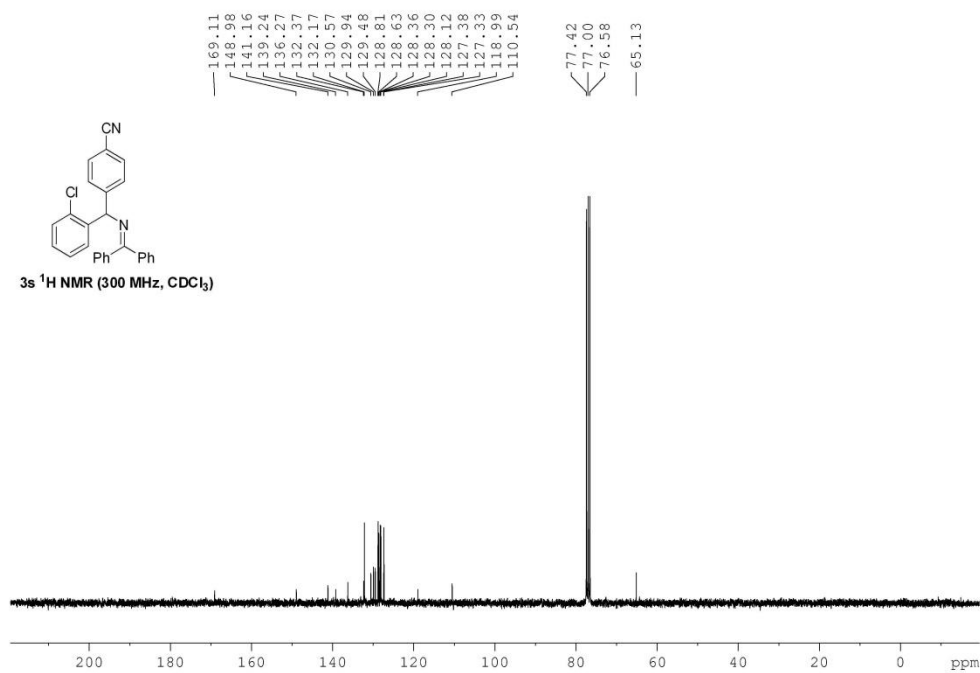
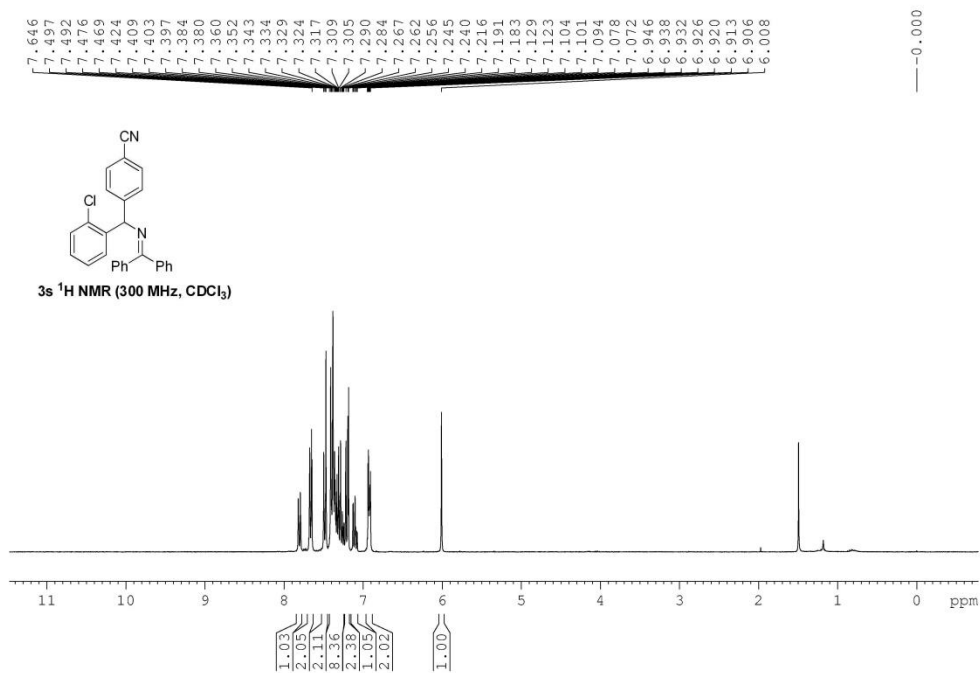


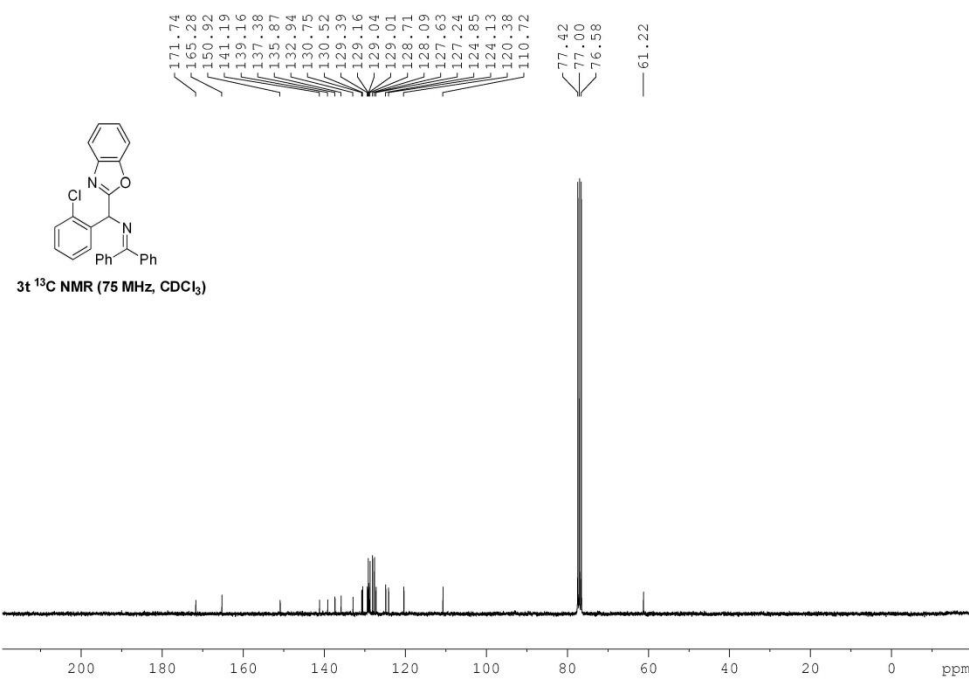
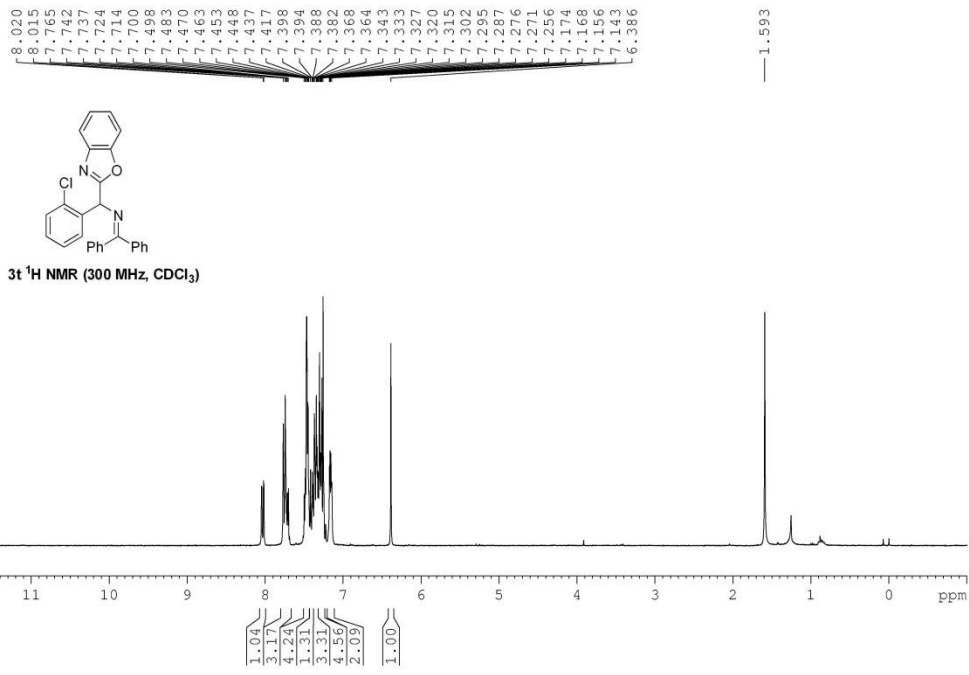


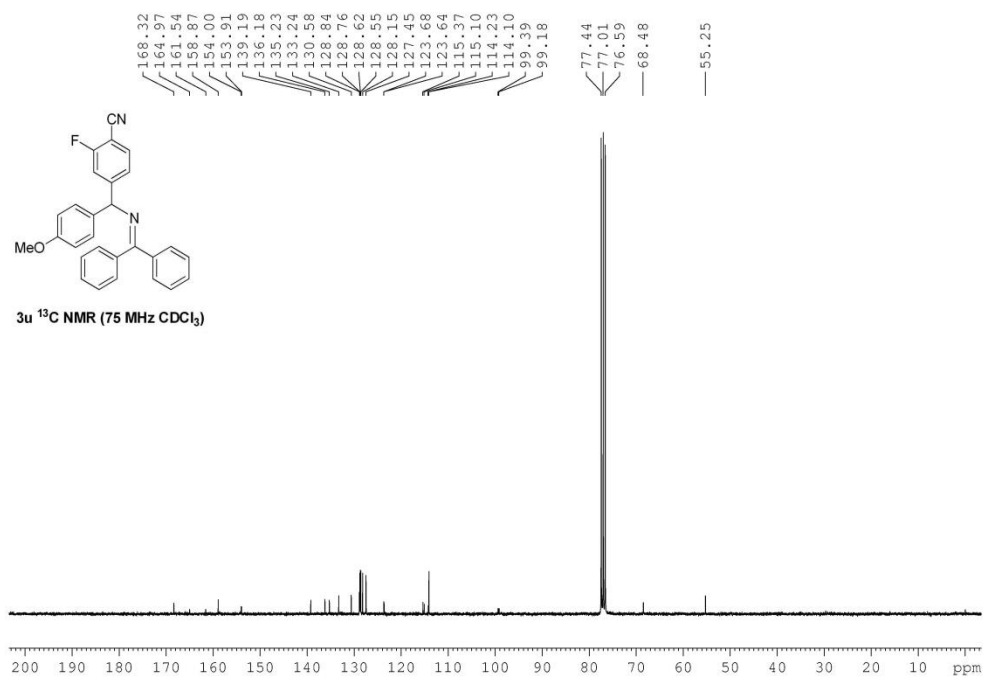
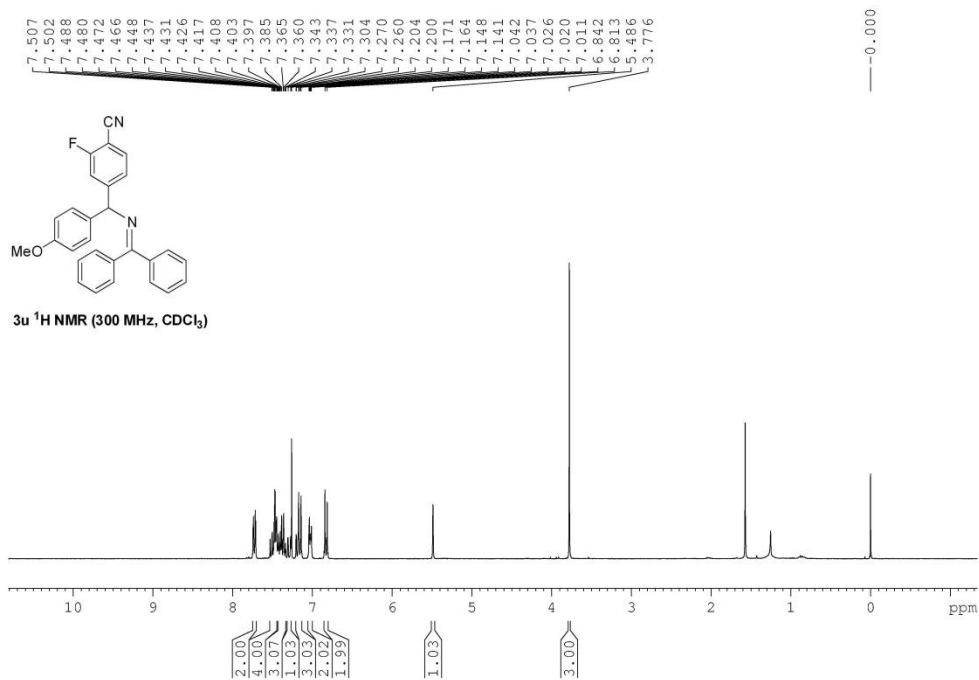


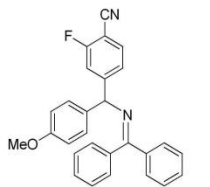




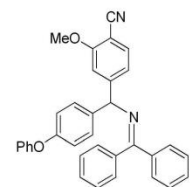
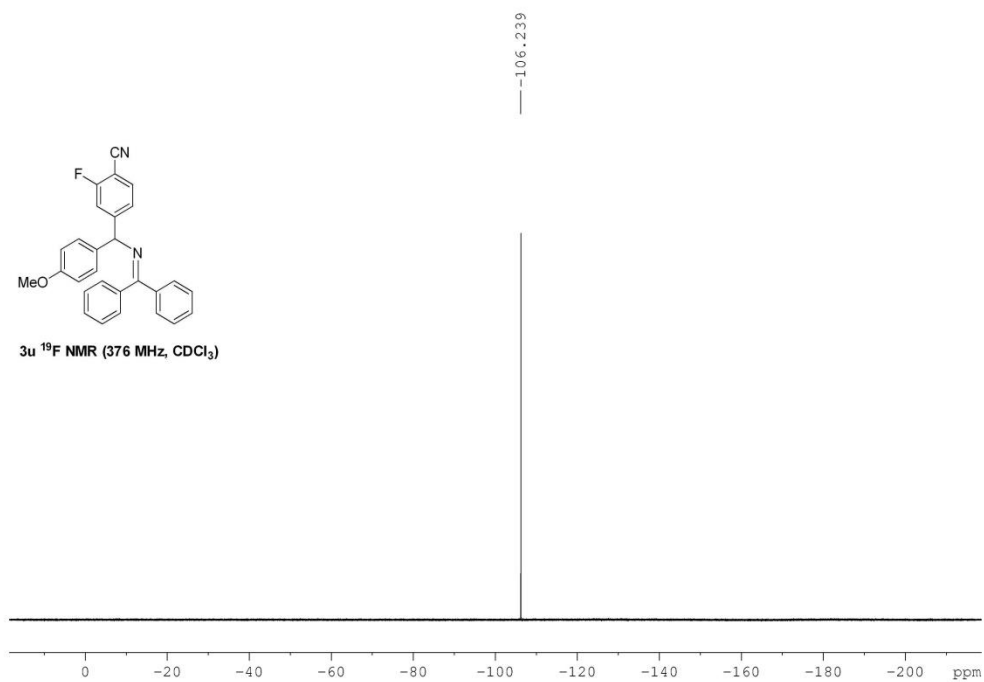








3u ¹⁹F NMR (376 MHz, CDCl₃)



3v ¹H NMR (300 MHz, CDCl₃)

